Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume II: Metals and Non-Volatile Organic Compounds
Section 3 - Benzo(a)pyrene

Prepared by:

Yoram Cohen
Department of Chemical Engineering
National Center for Intermedia Transport Research

Arthur M. Winer
Environmental Science and Engineering Program
School of Public Health

Research Associate:

Joanna Chu
Environmental Science and Engineering Program
School of Public Health

University of California, Los Angeles
Los Angeles, California 90024

ABSTRACT

An information base was developed on the physicochemical and transport parameters of benzo(a)pyrene which can be used for the purpose of multipathway exposure risk assessments. The environmental literature relevant to benzo(a)pyrene (B(a)P) was critically reviewed to: (1) determine the intermedia transfer factors relevant to B(a)P; (2) evaluate measured values of intermedia transfer factors; and (3) recommend estimation techniques for intermedia transfer factor applicable to B(a)P for use in the absence of measured values.

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1.0 INTRODUCTION AND BACKGROUND

1.1 Overview

The assessment of health risk requires the determination of exposure of the human receptor to pollutants from multiple pathways. The movement of chemicals throughout the environment is particularly important to the overall assessment of the exposure to toxic air pollutants since airborne pollutants can be deposited to the soil and water, and can be accumulated in plants and animals. Determination of air toxic contaminant concentrations can be obtained by either pollutant transport modeling or field measurements. Both approaches require an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants through environmental media.

Risk assessment is often accompanied with uncertainties which arise from the lack of data in various areas leading to reliance on assumptions and default values. Generally, the assumptions employed and the use of default values are designed to err on the side of human health protection to avoid underestimating risk to the public (e.g., CAPCOA Guidelines, 1992). Major sources of uncertainty in multimedia risk analysis for toxic air pollutants include:

- Extrapolation of toxicity data in animals to humans;
- Air dispersion modeling;
- Estimation of emissions; and
- Analysis of multimedia exposure.

This study addresses the final major source of uncertainty listed above, analysis of multimedia exposure. By identifying the input intermedia transfer factors most critical to multimedia exposure analysis and critically evaluating measured values and estimation techniques, this report should help characterize the uncertainty associated with estimating risk from multimedia exposures to benzo(a)pyrene. A summary of representative values and estimation methods for intermedia transfer parameters for B(a)P is given in Table 1-1. Although the calculated values presented only apply to specific conditions, representative values have been included for comparison purposes. Finally, a discussion of the various intermedia parameters and estimation methods are discussed in Sections 2-5.

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Multimedia Assessment of Benzo(a)pyrene

Parameter	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Section in Text
S	1.5×10^{-8}	mol/L	±8%	298	Measured	Mackay and Shiu, 1977	4.1.1
P_{vp}	7.3×10^{-7}	Pa	35-55%	298	Measured	Murray et al., 1974	4.1.2
ρ	1.351	g/cm^3	NR	293	NR	Kronberger, 1944	4.1.3
T_{MP}	176.4	°C	±1%	NA	Measured	Murray et al., 1974	4.1.4
V_b	2.63×10^{-1}	g/mol	NR	b.p.(a)	Estimated	Miller et al., 1985	4.1.5
T_{BP}	494	°C	NR	NA	Estimated	White, 1986	4.1.6
MW	252.32	g/mol	NR	NA	NR	IARC, 1973	4.1.7
ΔH_v	71.06	KJ/mol	NR	NR	Estimated	White, 1986	4.1.8
H	2.47×10^{-1}	$Pa \cdot m^3/mol$	NR	298	Measured	Southworth, 1979	4.2.1
log K_{ow}	5.99	Unitless	±1%	296	Measured	Mallon and Harrison, 1984	4.2.2
log K_{oc}	5.06-6.74	Unitless	NR	298	Estimated	See Section 4.2.4	4.2.4
BCF	See Table 4-9 for measured and estimated values corresponding to specific experimental conditions						4.2.5
B_{vd}	0.013	Unitless	NR	NR	Estimated(b)	Travis and Arms, 1988	4.2.5
B_{vw}	------	Unitless	NR	NR	Estimated(c)	Briggs et al., 1982	4.2.5
B_{vsw}	2.1×10^{8}-4.7×10^{8}	Unitless	NR	NR	Estimated(d)	See Sction 4.2.5	4.2.5

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Multimedia Assessment of Benzo(a)pyrene

(Continued)

Parameter	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Section in Text
B_m	7.69×10^{-3}	Unitless	NR	NR	Estimated(e)	Travis and Arms, 1988	4.2.5
B_b	0.025	Unitless	NR	NR	Estimated(f)	Travis and Arms, 1988	4.2.5
D_{air}	0.05034	cm^2/s	7.6% (Absolute average error)	298	Estimated(g)	Reid et al., 1977	4.3.1
D_{water}	5.684×10^{-6}	cm^2/s	5.8% (Absolute average error)	298	Estimated(h)	Reid et al., 1977	4.3.1
$V_d^{(+)}$	0.09-2.19	cm/s	NR	NR	Estimated(i)	See Section 4.3.3.1	4.3.3.1
$V_{(vapor)}$	See Section 4.3.3.1						
Degradation parameters							
$\tau_{1/2\ air}$	See Table 4-13 for values corresponding to specific conditions						4.4.1
$\tau_{1/2\ water}$	See Table 4-14 for values corresponding to specific conditions						4.4.2
$\tau_{1/2\ biodegradation}$	See Table 4-15 for measured values corresponding to specific conditions						4.4.3

NA = Not Applicable.
NR = Not Reported.
(+) particle-bound B(a)P

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Multimedia Assessment of Benzo(a)pyrene

(Continued)

(a) At the normal boiling point.

(b) $\log B_v = 1.588 - 0.578 \log K_{ow}$

(c) $B_{vw} = (0.82 + 0.028\ K_{ow}^{0.77})/K_d$; $K_d = K_{oc}\chi$; note that the value of B_{vw} depends on the soil organic content.

(d) Equations 4-28 and 4-29

(e) $\log B_m = -8.056 + 0.992 \log K_{ow}$

(f) $\log B_b = -7.6 + \log K_{ow}$

(g) Equation 4-50

(h) Equation 4-45

(i) Estimated based on field data for particle size distribution and B(a)P distribution in the particle phase.

1.2 Benzo(a)pyrene

Benzo(a)pyrene belongs to a class of compounds known as polycyclic aromatic hydrocarbons (PAH). Polycyclic aromatic hydrocarbons are generated as a result of incomplete combustion of coal, oil, gas, and other organic materials (U.S. PHS, 1990).

Among the PAHs, benzo(a)pyrene, hereinafter referred to as B(a)P, has been studied extensively worldwide due to its high toxicity and carcinogenicity (Cook et al., 1933; U.S. PHS, 1990, Pucknat, 1981; Harvey, 1985; Hoffman and Wynder, 1976). Figure 1.1 shows its chemical structure.

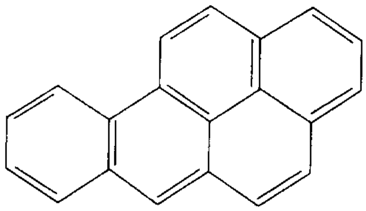

Figure 1.1. Chemical structure of benzo(a)pyrene.

Anthropogenic emission of B(a)P into the atmosphere in the U.S. was estimated to be approximately 1320 tons/year (Lo and Sandi, 1978). The Bay Area Air Quality Management District estimated the 1992 total state-wide emission in California to be 246 lb/yr, of which 220 lb/yr came from the South Coast Air Quality Management District (Bode, 1993).

B(a)P is a five-membered ring formed during the combustion of fossil fuels and plant or animal material. For example, the burning of gasoline or municipal solid waste incineration leads to the formation and release of B(a)P (U.S. PHS, 1990). B(a)P exists as a solid crystalline at room temperature. The crystals exist as plates or needles of pale yellow color (IARC, 1983; Weast, 1987). B(a)P has a very low solubility and vapor pressure.

In air, B(a)P is present mostly sorbed to particulate matter. It has been shown that B(a)P has a high propensity to adsorb onto coal fly ash (also known as soot) (Yokley et al., 1985). Following the release of B(a)P into the atmosphere, it can be transferred into the vegetation, soil, and water by a variety of intermedia transport processes as indicated schematically in Figure 1.2. In this manner, B(a)P becomes integrated into the biosphere and its transport and fate are governed by multimedia interactions.

1.3 Exposure Pathways of B(a)P

1.3.1 Overview

The major B(a)P exposure pathways are inhalation, ingestion, and dermal absorption. In indoor environments, B(a)P exposure pathways can increase relative to outdoor due to additional indoor B(a)P sources. For example, indoor background B(a)P levels have been shown to increase due to kerosene heaters and wood burning fireplaces. Dong and Bozzelli (1989) found that indoor background B(a)P concentrations measured during the winter season in a closed room were about 0.78 ng/m^3 with a standard deviation of ± 0.23 ng/m^3. After operation of a kerosene heater for 4 hrs, B(a)P concentration was reported to be 3.9 ng/m^3 with a standard deviation of ±0.27 ng/m^3. Even after the heater had been extinguished for 8 hrs, B(a)P levels remained elevated at 1.3 ng/m^3 with a standard deviation of ±0.21 ng/m^3. Also, it was shown that an open-wall fireplace led to an increase in the indoor B(a)P concentration from an ambient level of 0.16 ng/cm^3 to 3.5 ng/m^3, with a standard deviation of ±1.5 ng/m^3, where the heater was allowed to remain in operation for 8 hrs, 12 hrs and 24 hrs (Dong and Bozzelli, 1989).

Exposure to B(a)P can also occur due to cigarette and cigar smoke (i.e., active and passive smoking) (Tomkins et al., 1985; Appel et al., 1990). For example, Appel et al. (1990) reported average concentrations of B(a)P in cigar and roll-your-own (RYO) cigarette smoke to be 42 ± 7 and 48 ± 4 ng/g, respectively. In addition, the puff B(a)P concentration averaged about 60 μg/m^3 for cigars and RYO cigarettes. It is also known that B(a)P concentration in food may be increased while cooking food at high temperature [e.g.,

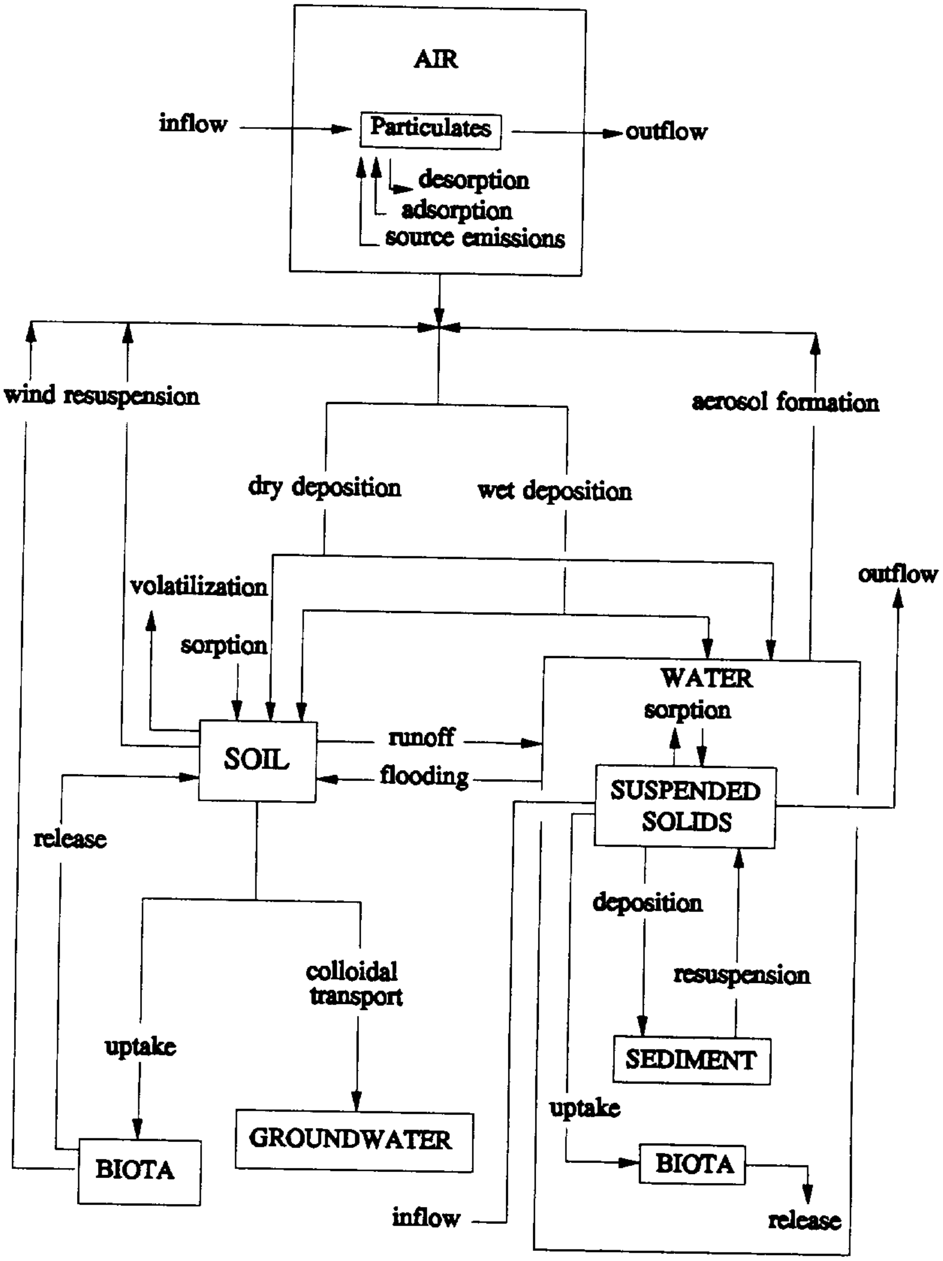
AIR
inflow
Particulates
outflow
desorption
adsorption
source emissions
wind resuspension
aerosol formation
dry deposition
wet deposition
volatilization
sorption
outflow
WATER
sorption
SOIL
runoff
flooding
SUSPENDED SOLIDS
release
deposition
resuspension
colloidal transport
uptake
SEDIMENT
uptake
GROUNDWATER
BIOTA
BIOTA
inflow
release

Figure 1.2. Schematic of Multimedia Transport Processes of Particle-Bound Pollutants

barbecuing or charring foods (U.S. PHS, 1990), and smoking, curing, or broiling over a direct flame (Lioy et al., 1988)].

Finally, occupational exposure to B(a)P can also be significant in some cases. For example, high B(a)P concentrations are associated with activities such as coal-tar production, coking, asphalt-production, coal-gasification, municipal trash incineration, and in most facilities that burn oil, wood, or coal (National Academy of Science, 1972; Lloyd, 1971).

1.3.2 Inhalation

Lioy et al. (1988) conducted a study on total human environmental exposure to B(a)P. They reported the average daily indoor exposure to B(a)P by inhalation to range from 9.2±8.0 to 39.3±37.7 ng/day for samples collected from ten homes in the proximity of a grey-iron pipe foundry located in Phillipsberg, New Jersey. They also reported an outdoor exposure to B(a)P by inhalation to range from 0.9 to 4.1 ng/day. The high exposure to B(a)P in the community was attributed, in part, to residential space heaters and cigarette smoke.

1.3.3 Ingestion

Contamination of food by B(a)P during processing and packaging can lead to exposure to B(a)P by ingestion. For example, Lo and Sandi (1978) reported that when hexane was used as a solvent to extract edible vegetable oils, B(a)P was found to be present at 21 ppb in the sample. Exposure to B(a)P can also occur due to ingestion of seafood from polluted waters. For example, Lo and Sandi (1978) reported that oysters collected from petroleum oil contaminated waters contained 2 to 6 ppb of B(a)P. Clams in the same areas may contain up to 16 and 25 ppb of B(a)P, compared to 1.5 ppb of B(a)P from "unpolluted" areas. It has also been shown that the presence of B(a)P in estuaries is reflected by the presence of B(a)P in fish bile in these estuaries (Johnston and Baumann, 1989). Lemaire et al. (1990) showed that the half-life of B(a)P ingested through feed was 2.4 days in sea bass.

Andelman and Suess (1970) reported that B(a)P was present in various processed foods such as fried, grilled, roasted, and smoked fish and meat product as well as in coffee. They reported levels of B(a)P to be 37 μg/kg in smoked fish and 200 μg/kg in coffee soot. Lioy et al. (1988) reported a weekly food ingestion of B(a)P to range from 10 to 4005 ng for homes near a metal pipe foundry in Phillipsberg, New Jersey. The authors concluded that a significant source of B(a)P was from cooking food at high temperatures.

1.3.4 Dermal Absorption

There are no data pertaining to the health effects of short-term dermal exposure of humans to B(a)P but there are a number of studies on animals. For example, laboratory experiments in which rabbit and mouse epithelial tissues were exposed to tobacco smoke condensate have demonstrated carcinogenicity (Wynder et al., 1953; Levin et al., 1976). It is worth noting that Andelman and Suess (1970) reported that B(a)P was highly potent for causing skin cancer in mice, but not so in rabbits. It is yet unclear from the above studies whether B(a)P is adsorbed onto the skin or absorbed through the skin.

1.3.5 Metabolism and Elimination

After it enters the body, B(a)P is rapidly distributed to the bronchus, colon, kidney, liver, lung, etc., and metabolized (U.S. PHS, 1990). B(a)P is metabolized initially by the microsomal cytochrome P-450 monooxygenase system to several arene oxides and subsequently to the ultimate carcinogen B(a)P 7,8-diol-9,10-epoxide (Levin et al., 1982; Cooper et al., 1983; Ribeiro et al., 1985).

Regardless of the route of entry, hepatobiliary excretion and fecal elimination of B(a)P occur after metabolism. However, B(a)P and its metabolites are reabsorbed by enterohepatic circulation before elimination (Chipman et al., 1982). The exposure route affects the time for B(a)P to be excreted in the following manner: dermal ≥ inhalation ≥ ingestion (U.S. PHS, 1990).

2.0 OBJECTIVES

The overall objective of this report is to present information on the intermedia transfers of benzo(a)pyrene which is pertinent for multimedia exposure pathways estimation and for health risk assessments. The purpose of this report is to: (1) critically review existing literature to determine pertinent intermedia transfer parameters for B(a)P; (2) evaluate and update intermedia transfer factors currently used in multimedia exposure estimations; and (3) provide pollutant-specific estimates where no data are available or where default values are used.

3.0 METHODOLOGY

In this study, an evaluation was conducted of the important parameters that are relevant for the determination of the behavior of B(a)P in various media and the food chain after its release into the atmosphere from stationary and mobile sources. Reported values for the selected parameters were collected and evaluated. In cases where there is a wide range of values reported from different studies, the research methods were evaluated to determine the most reliable values for the parameter of interest. The estimation techniques were critically reviewed for those parameters with no reported values. Since the results of this study may be used to support efforts in multipathway analysis of exposure to B(a)P, a number of multimedia contaminant transport models were reviewed in terms of algorithms, default values, underlying assumptions, and the influence of the overall logic on the estimates of risk.

3.1 Literature Review

A literature search using UCLA Melvyl, Pollution Abstracts, Enviroline, CAS, the Scientific Citation Index published by the Institute for Scientific Information (ISI), and the National Center for Intermedia Transport Research (NCITR) database was conducted. In addition, an extensive database was obtained from Dr. Douglas Lane of Environment Canada (personal communication). Through this process, references pertaining to the physicochemical properties, intermedia transport, and biotransformation of B(a)P were identified, obtained, reviewed, and summarized. The literature evaluation emphasized measured values. Where no measured values were found in the literature, estimation techniques applicable to B(a)P or homologous compounds were used.

3.1.1 Nomenclature

The nomenclature applied to polynuclear aromatic compounds has not been consistent over the years (Dipple et al., 1984) nor uniform internationally. As a result, there is a considerable degree of confusion in the literature especially with respect to particular compounds such as B(a)P. The ambiguity stems from different peripheral numbering systems (Pucknat, 1981; Dipple et al., 1984). For example, the compound of interest in this study, carcinogenic benzo(a)pyrene, was named 3,4-benzpyrene by American scientists and 1,2-benzpyrene by European scientists. However, the noncarcinogenic isomer, benzo(e)pyrene, B(e)P, was named 1,2-benzpyrene by American scientists and 4,5-benzpyrene by European scientists. Figures 3.1 to 3.4 illustrate the ambiguity: Figures 3.1 and 3.2 show the structures of B(a)P and B(e)P, respectively, and Figures 3.3 and 3.4 depict the American and the European systems, respectively.

The most recent accepted nomenclature is from the International Union of Pure and Applied Chemistry (IUPAC) and the Chemical Abstract Service (Pucknat, 1981; Dipple et al., 1984). The numbering rules are as follows:

(1) The maximum number of rings lie in a horizontal row;

(2) As many rings as possible are above and to the right of the horizontal row; and

(3) If more than one orientation meets these requirements, the one with the minimum number of rings at the lower left is chosen.

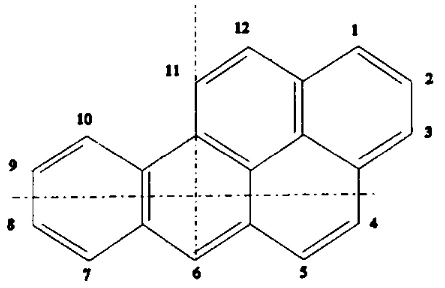
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Figure 3.1. Chemical Structure of (1) Benzo(a)pyrene, (2) 1,2-Benzpyrene, (3) 3,4-Benzpyrene *(carcinogenic)*

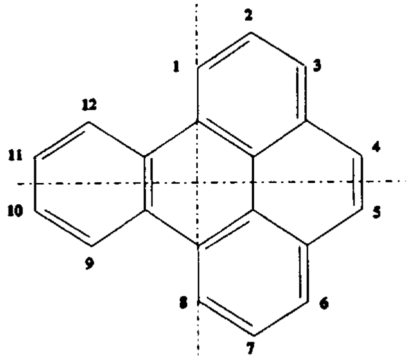
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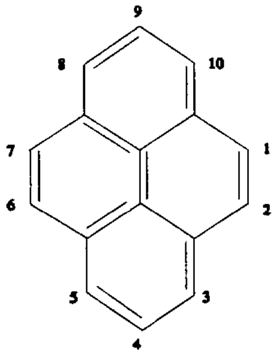
Figure 3.2. Chemical Structure of (1) Benzo(e)pyrene, (2) 4,5-Benzpyrene, (3) 1,2-Benzpyrene *(noncarcinogenic)*


9
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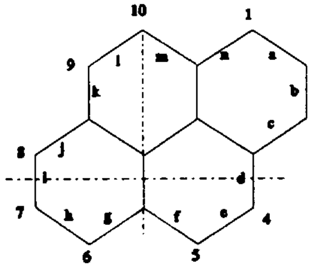
4

Figure 3.3. Chemical Structure of Pyrene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1
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3
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5

Figure 3.4. Chemical Structure of Pyrene

Reference: Dipple et al., 1984

In conducting a literature search for B(a)P, a number of synonyms were encountered in the literature. Table 3-1 lists the names cited in the literature along with their Chemical Abstract Service (CAS) registry numbers. In addition, each name has been assigned to a number from 1 to 10. These numbers are used to identify the reported names in the presentation of data (as superscripts in the References and Source Cited columns) in the tables of Section 4 of this report.

Since the names 3,4-benzpyrene and 3,4-benzopyrene are used only for B(a)P, one can be confident that when these names are cited in the literature, they correspond to B(a)P. However, with 1,2-benzpyrene or 1,2-benzopyrene, one can only be confident of the identity of the compound if the structure is given in the literature. Finally, it appears that there is no reliable way of determining which isomer is referred to by the authors when the name benzopyrene is encountered in the literature.

3.2 Selection of Parameters

In order to provide a critical review of intermedia transfers, a number of input parameters were considered. The final selection was based on the chemical and physical interpretation of the input parameters, their applicability to different classes of pollutants, and measures of the environmental consequences of intermedia transfers. The following subsections discuss the rationale for selecting input parameters as well as general limitations in their use.

3.2.1 Physicochemical Parameters

The physicochemical properties of B(a)P are important for the analysis of intermedia transport parameters such as mass transfer coefficients and for the determination of parameters such as partition coefficients and biotransfer factors. Chemical properties that are used to evaluate parameters such as partition coefficients and solubility.

Table 3-1. Nomenclature of Benzo(a)pyrene

Name of the Compound	CAS Registry #	Designation
Benzo(a)pyrene	50-32-8	1
3,4-Benzpyrene	50-32-8	2
3,4-Benz[a]pyrene	50-32-8	3
Benzopyrene	50-32-8	4
3,4-Benzopyrene	50-32-8	5
Benzo(e)pyrene	192-97-2	6
1,2-Benzpyrene	192-97-2	7
1,2-Benzopyrene	192-97-2	8
Benzopyrene	73467-76-2	9
4,5-Benzpyrene	50-32-8	10

A review of a number of multimedia models including SMCM, Fugacity and GEOTOX (see Cohen, 1986), as well as the CAPCOA Risk Assessment Guidelines, 1992, suggested that the major physicochemical factors required for conducting a multimedia exposure assessment for B(a)P are as follows:

- Water Solubility;
- Vapor Pressure (as a function of temperature);
- Density;
- Molar Volume;
- Boiling Point;
- Molecular Weight;
- Melting Point; and
- Heat of Vaporization.

The definition of these parameters and the results of the literature review are presented in Section 4.1.

3.2.2 Partition Coefficients

Once B(a)P is released into the environment, it will be distributed to various compartments due to various transport processes. The net transport of B(a)P from one compartment to another may be limited, in part, by equilibrium constraints which are quantified by appropriate partition coefficients. The partition coefficient, H_{ij} is generally defined as

$$H_{ij} = C_i/C_j \tag{3-1}$$

where C_i and C_j are the concentration in compartment i and j, respectively, at equilibrium. In this report, the following partition coefficients for B(a)P were considered:

- Henry's Law Constant;
- Octanol-Water Partition Coefficient;
- Gas Phase/Particle Partitioning Coefficient;
- Soil/Water-Organic Carbon Partition Coefficient; and
- Bioconcentration Factors.

It is noted that bioaccumulation factors and bioconcentration factors often represent steady-state concentrations rather than equilibrium state. These factors are also at times based on total concentrations which include particle-bound and dissolved B(a)P; thus, in such cases, the reported coefficients do not represent thermodynamic constraints and simply represent the partitioning obtained for the particular experimental conditions involved.

3.2.3 Intermedia Transport Parameters

The transport of B(a)P in the environment is governed by either convective transport in a given medium (not addressed in this report) or intermedia transport from one environmental compartment to another. It is important to note that since it is a semivolatile organic (Bidleman, 1988; Venkataraman, 1992), B(a)P which is emitted to the atmosphere is present in both the gaseous and particle-bound forms. Thus, the exchange of B(a)P between the atmosphere and the terrestrial and aquatic environments depends on the dry and wet deposition of gaseous and particle-bound forms of B(a)P, as well as on wind resuspension. The literature reviewed suggests that the major relevant intermedia transfer parameters for B(a)P are as follows:

- Diffusion Coefficients in Air and Water;
- Mass Transfer Coefficients for Air/Water Exchange;
- Dry Deposition Velocity;
- Precipitation Scavenging;
- Colloidal Transport in Soils and Sediment/Water; and
- Biotransfer Factors.

These intermedia transport parameters are defined and discussed in Section 4.3. In addition, available information on bioavailability and pharmacokinetics of B(a)P and the implication for its accumulation in biological receptors is briefly discussed in Section 4.2.7.

3.2.4 Degradation Processes

Reactions for individual abiotic and biotic degradation processes involve chemical- and medium-specific transformations. Environmental reactions are often expressed as the first or "pseudo-first" order reaction rates. The first order reaction rate constants are often reported as degradation half-lives for soil, water, and air. It is important to note that these half-lives do not account for intermedia transport of a chemical and are, therefore, not representative of a chemical's actual persistence within a particular environmental medium. The degradation processes considered for assessing the transformation of B(a)P in the environment are listed below.

- Photooxidation Rate/Half-life in Air (including adsorbed on particulate);
- Photolysis Rate/Half-Life in Air (including adsorbed on particulate);

- Photolysis Rate/Half-life in Water;
- Biodegradation Rate/Half-Life in Water; and
- Biodegradation Rate/Half-Life in Soil.

The above degradation processes are briefly discussed below with an extended discussion and presentation of the reported half-lives given in Section 4.4. It is noted that one often encounters in the literature reported half-lives that are derived based on combined degradation and transport processes. These type of half-lives are termed here, overall half-lives and are discussed in Section 4.4.

Photooxidation in air: It is known that the chemical loss processes for organic compounds present in the atmosphere, in the gas phase, primarily involve photolysis and chemical reaction with OH and NO_3 radicals and with O_3, with the OH radical reaction being the most important of these loss processes for the majority of organic compounds. The rate constants for reaction of OH and NO_3 radicals and O_3 with B(a)P have not been experimentally measured because of the low vapor pressure of this compound.

Biodegradation in water and soil: Biodegradation is an important environmental process responsible for the breakdown of environmental compounds. It is a significant loss mechanism in soil and aquatic systems and plays an important role in wastewater treatment. Lu et al. (1977) reported that B(a)P was very resistant to soil microbial degradation under laboratory conditions. However, degradation of B(a)P by various soil microflora has been reported (Poglazova et al., 1971).

Photolysis in air and water: Half-lives for direct photolysis are based on irradiation of a chemical in solution at environmentally important wavelengths (>290 nm). Photolysis rates in air are generally assumed to equal to those in solution. The typical frequencies of maximum absorption, λ_{max}, and whether or not absorption occurs at wavelengths >290 nm may indicate whether a chemical has the potential to undergo photolysis in the environment. The photolysis half-life of B(a)P in air is reported to be about three to six days (U.S. EPA, 1986; Zepp and Schlotzhauer, 1979).

Photooxidation reactions with alkylperoxy (RO_2), hydroxyl radicals (OH) or singlet oxygen ($^1O_2$) in water: For some chemical classes, reactions with photooxidants in sunlit waters can be important. As with photooxidation in air by OH radicals, the range of half-lives is calculated from reaction rate constants and monitored concentrations of oxidants in relatively oligotrophic and eutrophic natural waters. No data for the photooxidation half-life of B(a)P have been reported and this degradation process is not considered in this report.

Hydrolysis in water and soil: Hydrolysis only applies to a limited number of chemicals that have hydrolyzable functional groups such a esters, aliphatic halogens, amides, carbamates, and phosphate esters. Since B(a)P does not contain hydrolyzable functional groups, hydrolysis is not a relevant degradation process.

Studies on degradation of B(a)P in different environmental media often report values for half-lives without determining specific loss mechanisms involved. Thus, when loss mechanisms are not apparently in a given reference, then the reported half-lives are assumed to be overall half-lives that account for both reaction and transport.

4.0 PRESENTATION OF RESULTS

The following subsections define, discuss, and summarize the findings of the literature search for each of the parameters reviewed in this study. Equations defining intermedia transfer parameters and estimation techniques are presented, where appropriate.

Values found in the literature for the intermedia transfer parameters are summarized in Tables 1-1 and 4-1 through 4-15. The data in these tables are arranged by decreasing order of reliability. Measured values of known uncertainty are listed first. Measured values reported without estimates of uncertainty are listed next, followed by calculated or estimated values reported with the corresponding prediction equations and uncertainty estimates. Values reported without their associated estimation equations were reported last. The superscripts immediately following the year in the Reference and the Source Cited columns denote the original name used for B(a)P in the literature. See Table 3-1 for the number assignments.

Values from references for which the derivation of the results could not be ascertained and multiple references to the same measured value are listed below the dotted line in the summary tables. The scientific confidence in these results is clearly limited; they have been included only to reflect the range of values commonly reported in the current environmental literature. Values for input parameters have been converted to consistent SI units to facilitate comparison of results. The converted values have been reported with the same number of significant figures as the values reported in the corresponding reference. Specific conversion equations are shown in the tables. It should be noted that commonly used forms of estimation equations often require input parameters in non-SI units. These cases have been identified in the text following presentation of the appropriate equations.

4.1 Physicochemical Parameters for B(a)P

Section 4 describes the general need for using physicochemical parameters in multipathway assessment. This section further defines the specific physicochemical parameters that are needed for multimedia transport and exposure analysis of pollutants and discusses the results of the literature review.

4.1.1 Solubility in Water

The aqueous solubility (S) of a chemical is defined as the maximum amount of the chemical that will dissolve in pure water at a specific pressure, temperature and pH. The units of aqueous solubility are usually stated in terms of weight per weight (ppm, ppb, g/kg, etc.) or weight per volume (mg/L, g/L, mol/L, etc.). Less common units are mole fraction and molal concentration (moles per kg solvent). In this report solubility is given in mol/L to be consistent with SI units. Values for the water solubility of B(a)P found in the literature are summarized in Table 4-1. Most solubility data were reported in 25°C.

Mackay and Shiu (1977) reported the solubility of B(a)P in distilled water at 25°C to be 0.0038 mg/L (or 1.5×10^{-8} mol/L) with an uncertainty of ±0.00031 mg/L. The solubility was determined from a saturated aqueous B(a)P solution made with doubly distilled water. The solution was stirred for 24 hours and allowed to settle for at least 48 hours at 25°C. The suspended particles in the solution were removed by a 5 μm Millipore filter before extraction with cyclohexane. The cyclohexane extract was analyzed using an Aminco-Bowman spectrophotofluorometer. The authors reported a 5% to 10% error in replicate solubility measurements.

Lu et al. (1977) reported the solubility of B(a)P to be 0.172 ppb (or 6.8×10^{-10} mol/L) at 25°C. However, the experimental method was not reported, and the reported solubility is significantly lower than the value reported by Mackay and Shiu (1977).

Locke (1974) used the solubility of benzene and fluoranthene in water at 20°C and established a log (liquid chromatographic retention time) versus log (inverse solubility) plot. From this plot, the solubilities of seven PAHs were either interpolated or extrapolated. B(a)P was among one of the PAHs used in the correlation and the solubilities of B(a)P were estimated from the plot by using four retention times. The solubilities ranged from 1.5×10^{-10} to 2.4×10^{-10} mol/L, which is lower by about 2 orders of magnitude than the majority of the B(a)P solubility data reported in the literature. The authors did not provide a satisfactory explanation for their results, and one is led to believe that accuracy of the experimental method is questionable.

In an earlier study, Barone et al. (1966) reported a B(a)P solubility of 1.9×10^{-8} mol/L at 25°C. This value is very close to the value reported by Mackay and Shiu (1977). However, the experiments were conducted with unneutralized poly(methacrylic acid) (PMA) aqueous solutions instead of distilled water. Thus, the solubility reported by Barone et al. (1966) is a value extrapolated to pure water from data for PMA solutions.

Boyland and Green (1962) measured the solubility of polycyclic hydrocarbons in caffeine solutions at 22°C, and these values were then corrected for the solubility of the

Table 4-1. Solubility[1] of Benzo(a)pyrene in Water*

Solubility in Water (mol/L)	Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	Reference	Source Cited
1.5×10^{-8}(a),(b),(c)	0.0038 1.5×10^{-5}	g/m^3, mg/L mol/m^3	±0.00031 mg/L	25°C	Experimental	Mackay and Paterson, 1991; Montgomery and Welkom, 1990; Bevan and Manger, 1985(1); Miller et al., 1985(5)	Mackay and Shiu, 1977(2)
1.9×10^{-8}	1.9×10^{-8}	mol/L	NR	25°C	Experimental	Barone et al., 1966(2)	
1.6×10^{-8}(d)	4.0	µg/L	±0.5 µg/L	27±3°C	Experimental°	Davis and Parke, 1942(2); Davis et al., 1942(2)	
2.4×10^{-8}(e)	0.024	µmol/L	NR	20°C	Experimental‡	Weil-Malherbe, 1946(2)	
9×10^{-9}(e)	0.009	µmol/L	NR	22°C	Experimental†	Boyland and Green, 1962(4)	
1.5×10^{-10}	1.5×10^{-10}	mol/L	NR	20°C	Experimental**	Locke, 1974(1)	
2.4×10^{-10}	2.4×10^{-10}	mol/L					
2.0×10^{-10}	2.0×10^{-10}	mol/L					
1.5×10^{-10}	1.5×10^{-10}	mol/L					
4.8×10^{-9}(f)	1.2	ng/ml	±0.1 ng/ml	22±2°C	Experimental	Montgomery and Welkom, 1990(1)	U.S. EPA, 1978(1)
6.8×10^{-10}(g)	0.172	ppb	NR	25°C	Experimental	Lu et al., 1977(1)	
1.2×10^{-8}(c)	0.003	mg/L	NR	NR	NR	Montgomery and Welkom, 1990(1)	Verschueren, 1983(1)
2.0×10^{-9}(c)	0.0005	mg/L	NR	25°C	NR	Eisenbrand, 1971(2)	

Table 4-1. Solubility of Benzo(a)pyrene in Water*
(Continued)

Solubility in Water (mol/L)	Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	Reference	Source Cited
$4.7\times10^{-8(e)}$	0.0472	µmol/L	NR	20°C	NR	Wilk and Schwab, 1968(2)	
$1.5\times10^{-8(h)}$	3.8×10^{-6}	g/L	NR	25°C	NR	U.S. PHS, 1990(1)	U.S. EPA, 1982(1)

NR = Not Reported.

[1] The water solubility of a chemical is defined as the maximum amount of the chemical that will dissolve at a specific temperature and pH.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

o Extrapolated.

‡ Corrected from purine solution.

† Corrected from caffeine solution.

** Extrapolated from the plot of log retention time versus log solubility^{-1} plot for benzene and fluoranthene.

(a) Conversion from reported value: $\mathbf{g/m^3} \times \frac{1\ \mathrm{m^3}}{10^3\ \mathrm{L}} \times \frac{1\ \mathrm{mol\ B(a)P}}{252.3\ \mathrm{g\ B(a)P}} = \mathrm{mol/L}$

(b) Conversion from reported value: $\mathbf{mol/m^3} \times \frac{1\ \mathrm{m^3}}{10^3\ \mathrm{L}} = \mathrm{mol/L}$

(c) Conversion from reported value: $\mathbf{mg/L} \times \frac{1\ \mathrm{mol\ B(a)P}}{252.3\ \mathrm{g\ B(a)P}} \times \frac{1\ \mathrm{g}}{1000\ \mathrm{mg}} = \mathrm{mol/L}$

(d) Conversion from reported value: $\mathbf{\mu g/L} \times \frac{1\ \mathrm{mol\ B(a)P}}{252.3\ \mathrm{g\ B(a)P}} \times \frac{1\ \mathrm{g}}{10^6 \mu\mathrm{g}} = \mathrm{mol/L}$

(e) Conversion from reported value: $\mathbf{\mu mol/L} \times \frac{1\ \mathrm{mol}}{10^6\ \mu\mathrm{mol}} = \mathrm{mol/L}$

(f) Conversion from reported value: $\mathbf{ng/ml} \times \frac{1\ \mathrm{mol\ B(a)P}}{252.3\ \mathrm{g\ B(a)P}} \times \frac{1\ \mathrm{g}}{10^9\ \mathrm{ng}} \times \frac{1000\ \mathrm{ml}}{\mathrm{L}} = \mathrm{mol/L}$

(g) Conversion from reported value: **ppb = µg/L calculated as (f)**

(h) Conversion from reported value: $\mathbf{g/L} \times \frac{1\ \mathrm{mol\ B(a)P}}{252.3\ \mathrm{g\ B(a)P}} = \mathrm{mol/L}$

compound in water. The authors reported a solubility of 0.009 μmol/L (or 9×10^{-9} mol/L) for benzopyrene. However, the authors did not specify which benzopyrene they studied; therefore, there is low confidence in this value.

Weil-Malherbe (1946) reported a solubility of 0.024 μmol/L at 20°C. However, the solubility was determined from B(a)P dissolved in a caffeine solution instead of in distilled water. The reported solubility was obtained from extrapolation of the solubility verse caffeine concentration curve, resulting in B(a)P solubility of 2.4×10^{-8} mol/L.

Davis et al. (1942) used the nephelometric method for solubility determination. The values from replicate experiments conducted at 27 ± 3°C ranged from 3.0 to 4.5 μg/L with an error of ± 0.5 μg/L. The average solubility value reported by the authors was 4.0 μg/L (or 1.6×10^{-8} mol/L), which is within 7% of the value reported by Mackay and Shiu (1977).

In addition to experimental values of B(a)P for solubility, Mackay and Shiu (1977) have suggested an estimation technique for calculating the aqueous phase solubility. Accordingly, the solubility of the organic compound, X_w, is given by

$$X_w = \frac{1}{\gamma_w^\infty}\left(\frac{f_s}{f_r}\right) \tag{4-1}$$

in which γ_w^∞ is the infinite dilution activity coefficient of the compound in the aqueous phase, f_s is the fugacity for the pure hydrocarbon, and f_r is the reference fugacity for the dissolved hydrocarbon. Equation 4-1 assumes that the solubility is low such that $X_w << 1$. The infinite dilution activity coefficient, γ_w^∞, can be estimated from (Pierotti et al., 1959):

$$\log \gamma_w^\infty = 3.5055 + 0.3417\,(N\text{-}6) - 0.002640\,(N\text{-}6)^2 \tag{4-2}$$

in which N is the carbon number. For chemicals that are liquids in their pure form, at the environmental conditions of interest $f_s = f_r$. However, for solid hydrocarbon, the ratio f_s/f_r can be estimated from the following correlation:

$$\ln\left(\frac{f_s}{f_r}\right) = K\ (T_p - 298.15) \qquad (4\text{-}3)$$

in which K is a constant estimated to be -0.02273 by Tsonopoulos and Prausnitz (1971) and T_p is the triple point temperature (K). Using the above approach, X_w (in mole fraction) is reported to be 2.73×10^{-10} for B(a)P.

4.1.2 Vapor Pressure as Cited in the Literature

The saturation vapor pressure, P_{vp}, is a measure of the volatility of a chemical in its pure state and it is an important determinant of the rate of vaporization and estimating various thermodynamic parameters (e.g., Henry's Law constant). Methods of estimating P_{vp} often require information on the following properties: (1) critical temperature; (2) critical pressure; and (3) heat of vaporization, and/or the vapor pressure at some reference temperature. The units of P_{vp} can be stated in atm, torr, mm Hg, or Pa. However, in this report, P_{vp} is given in units of Pascal (Pa).

Murray et al. (1974) measured the saturation vapor pressures of five polycyclic aromatic hydrocarbons using the Knudsen effusion weight loss method. B(a)P was among the five compounds measured. The experimental results over the temperature range of 358 to 431 K were described by the following equation:

$$\log_{10}[P_{vp}] = -(A/T) + B \qquad (4\text{-}4)$$

where A and B are empirical constants, and K is the temperature (K), and P_{vp} is the vapor pressure (atm).

The values of A and B for B(a)P were reported to be 6181 ± 32 and 9.601 ± 0.083, respectively. In this report, the range of the parameter values were used to illustrate the uncertainty of calculated vapor pressures of B(a)P at 298 K. The vapor pressures at 298 K ranged from 4.67×10^{-12} atm to 1.12×10^{-11} atm, with a mean value of 7.23×10^{-12} atm (or

7.3×10^{-7} Pa). The difference between the lowest and the mean vapor pressure is 35% and the difference between the highest and the mean vapor pressure is 55%. It is also noted that the mean vapor pressure of 7.3×10^{-7} Pa is cited by Hattemer-Frey and Travis (1991), Mackay and Paterson (1991), Verschueren (1983), Pucknat (1981), and U.S. EPA (1976). Pupp et al. (1974) also cited Eq. 4-4. However, these authors reported the parameter A to be 6182 K instead of 6181 K. As a result, the calculated vapor pressure using A = 6182 at 298 K is 7.18×10^{-12} atm. (or 7.25×10^{-7} Pa).

4.1.3 Density

The density (ρ) of a substance is the ratio of its mass to its volume with units of g/ml. The density varies not only with molecular weight but also with molecular interaction and structure. Density can be used to estimate molar volume of B(a)P, expressed in units of g/cm^3. The molar volume is a useful parameter in correlations used to estimate diffusion coefficients in air and water. Kronberger and Weiss (1944) reported the density of B(a)P at 20°C to be 1.351 g/cm^3.

4.1.4 Melting Point Temperature

The melting point of a pure substance is defined as the temperature at which its crystals are in equilibrium with the liquid phase at atmospheric pressure. T_{MP} can be also used in the prediction of other physicochemical properties such as vapor pressure and parameters such as K_{ow}. Table 4-3 lists the melting point values of B(a)P.

Cook et al. (1933) reported the melting point of their pure sample to be 176.5 to 177.5°C. They synthesized B(a)P from purifying 4'-Keto-1':2':3':4'-tetrahydro-1:2-benzpyrene. Fieser and Hershberg (1938) synthesized and purified B(a)P from 3-benzoylperinaphthane (total yield of about 50%) and determined the melting point of their product to be in the range of 176 to 177°C. Murray et al. (1974) reported the melting point of B(a)P to be 176.4°C with an error of < 2°C. The melting point temperature was obtained using a Mettler FP51 melting point apparatus.

Table 4-2. Vapor Pressure of Benzo(a)pyrene*

Vapor Pressure (Pa)	Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	Reference	Source Cited
7.30×10^{-7}(a)	7.23×10^{-12}	atm	35-55%	25°C	Experimental	Murray et al., 1974(1)	
7.25×10^{-7}(a)	7.18×10^{-12}	atm	NR	25°C	Experimental	Pupp et al., 1974(1)	Murray et al., 1974(1)
7.3×10^{-7}	7.3×10^{-7}	Pa	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	Mackay and Paterson, 1991; Verschueren, 1983(1)
7.4×10^{-7}(b)	5.6×10^{-9}	mm Hg	NR	25°C	NR	U.S. PHS, 1990(1)	U.S. EPA, 1982(1); Murray et al., 1974(1)
7.30×10^{-7}(b)	5.49×10^{-9}	mm Hg	NR	25°C	NR	Montgomery and Welkom, 1990(1)	U.S. EPA, 1976(1); Pupp et al., 1974(1)
7×10^{-7}(b)	5×10^{-9}	mm Hg torr	NR	25°C	NR	Montgomery and Welkom, 1990(1)	U.S. EPA, 1978(1)
6.6×10^{-7}(b)	5.0×10^{-7}	mm Hg	NR	20°C	NR	Montgomery and Welkom, 1990(1)	U.S. EPA, 1988(1)
7.28×10^{-7}(a)	7.21×10^{-12}	atm	NR	25°C	NR	NRC Secretariat, 1983	
7.30×10^{-7}(c)	5.49×10^{-9}	torr	NR	NR	NR	Pucknat, 1981(1)	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Conversion from reported value = $\textbf{atm} \times \frac{\textbf{101000 Pa}}{\textbf{1 atm}} = \textbf{Pa}$

(b) Conversion from reported value = $\textbf{mm Hg} \times \frac{\textbf{101000 Pa}}{\textbf{760 mm Hg}} = \textbf{Pa}$

(c) Conversion from reported value = $\textbf{torr} \times \frac{\textbf{1 atm}}{\textbf{760 torr}} \times \frac{\textbf{101000 Pa}}{\textbf{1 atm}} = \textbf{Pa}$

Table 4-3. Melting Point of Benzo(a)pyrene*

Melting Point (°C)	Reported Uncertainty	Technique	References	Source Cited
176.4	<2°C	Experimental	Murray et al., 1974(1)	
176	NR	Experimental	Barone et al., 1966(2)	
178.6 to 179.8	NR	Experimental	Egloff, 1947(7)	Bachmann et al., 1941(2)
176 to 177	NR	Experimental	Fieser and Hershberg, 1938(2)	
176.5 to 177.5	NR	Experimental	Cook et al., 1993(7)	
179 to 179.3	NR	NR	U.S. PHS, 1990; IARC, 1973; Montgomery and Welkom, 1990(1)	Weast, 1987(8)
177 to 178	NR	NR	NRC Secretariat, 1983	
177.8	NR	NR	Whitehouse and Cooke, 1982(1)	Weast, 1980-1981(8)
175 to 177	NR	NR	Aldrich Chemical Company, 1984(1)	
179	NR	NR	Pearlman et al., 1984(1); Verschueren, 1983(1)	Weast, 1977(8)
178.1	NR	NR	Jacob et al., 1984(1)	
177 - 180	NR	NR	Aldrich Chemical Company, 1990(1)	
175(a)	NR	NR	Mackay and Shiu, 1977(5)	
176.5	NR	NR	Mackay et al., 1980(5)	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Reported as triple points which are assumed by the authors to be melting points.

Barone et al. (1966) conducted experiments with polycyclic aromatic hydrocarbons and they reported the melting point of B(a)P to be 176°C. For their experiment, B(a)P was purified by repeated crystallization from benzene-ethanol (1:9) mixtures and the purity was confirmed by thin layer chromatographic analyses. However, the apparatus for the determination of the melting point was not described.

In an earlier study, Bachmann et al. (1941) synthesized B(a)P from cyclic ketone (prepared from unrecrystallized γ-3-pyrenylbutyric acid). After a series of purification and recrystallization, the melting point of their purest sample of B(a)P was determined to range from 179 to 180°C.

4.1.5 Molar Volume

The molar volume (V_b) of B(a)P, expressed in units of cm^3/mol, is the volume of a mole of liquid B(a)P at the normal boiling temperature. The molar volume of an organic liquid is a useful parameter because of it is used in various correlations of physicochemical properties, including correlations for estimating molecular diffusion coefficients in air and water. The molar volume of B(a)P at the boiling point was reported to be 263 cm^3/mol (or 2.63×10^{-1} L/mol) by Miller et al. (1985) using the Le Bas method (Reid et al., 1987).

4.1.6 Boiling Point Temperature

The boiling point temperature, T_{BP}, is defined as the temperature at which the vapor pressure of a liquid is equal to the total pressure above the liquid. For pure compounds, the normal T_{BP} is defined as the T_{BP} at one standard atmosphere of pressure on the liquid. T_{BP} provides an indication of the physical state and volatility of a chemical. T_{BP} can also be used to predict other physical properties such as critical temperature and enthalpy of vaporization.

Table 4-4. Molar Volume[1] (V_b) of Benzo(a)pyrene

Value (cm³/mol)	Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	Reference
263	263	cm³/mol	NR	boiling point	Calculated[†]	Miller et al., 1985(5)

NR = Not Reported.

[1] Molar volume is the volume of a mole of a liquid at the normal boiling temperature

[†] Le Bas method.

Table 4-5 lists the boiling point temperature of B(a)P for two pressure conditions. The T_{BP} values for 1 atmosphere or 760 mm Hg range from 494 to 496°C. Using published boiling temperatures of 114 PAH (Bjorseth, 1983, cited by White, 1986), White (1986) developed a linear relationship between his experimental gas chromatographic retention index and the boiling point temperature of different PAHs. The calculated T_{BP}, 767K (or 474°C) agrees well with the literature T_{BP} of 769K (or 476°C, Bjorseth, 1983). The T_{BP} values reported at a pressure of 0.013 atmosphere (or 10 mm Hg) range from 310 to 312°C (U.S. PHS, 1990; Verschueren, 1983).

4.1.7 Molecular Weight

The molecular weight is used for converting mass to concentration and in various correlations of transport properties such as diffusion coefficients. The molecular weight of B(a)P is 252.32 g/mol (IARC, 1973). Small difference among molecular weight values reported in literature is due to the number of reported significant figures.

4.1.8 Heat of Vaporization

The heat of vaporization, ΔH_v, is defined as the quantity of heat required to convert a unit mass of liquid into a vapor without a rise in temperature, under a constant pressure. Its most important use is in estimating other physicochemical properties and partitioning of a chemical between the gas and particle phases. White (1986) predicted ΔH_v of B(a)P to be 71.06 KJ/mol at boiling point using Trouton's rule (Reid et al., 1987).

4.2 Partition Coefficients for B(a)P

The specific definitions for the various partition coefficients and the reported values for the individual partition coefficients are presented in the following sections.

Table 4-5. Boiling Point Temperature (T_{BP}) of Benzo(a)pyrene*

Boiling Point (°C)	Reported Uncertainty	Conditions	Technique	References	Source Cited
494	NR	1 atm	Calculated	White, 1986(1)	
495	NR	760 mm Hg	NR	U.S. PHS, 1990; Montgomery and Welkom, 1990; Pearlman et al., 1984 (1)	Aldrich Chemical Company, 1986, 1988(1); Weast, 1977(8)
496	NR	1 atm	NR	Bjorseth, 1983(1)	
475	NR	760 mm Hg	NR	NRC Secretariat, 1983	
310-312	NR	10 mm Hg	NR	U.S. PHS, 1990(1)	Weast, 1987(8)
311	NR	10 mm Hg	NR	Verschueren, 1983(1)	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

4.2.1 Henry's Law Constant

The Henry's Law constant is an important parameter for the evaluation of chemical partition between air and water and is required as an input parameter in most multimedia models. The Henry's Law constant for a given chemical (H_i) is defined as:

$$H_i = P_i / C_i \tag{4-5}$$

where P_i is the partial pressure of the contaminant (e.g., Pa) at the system temperature, and C_i is the concentration (e.g., mol/m^3) of the chemical in the aqueous phase in equilibrium with the air phase. The Henry's Law constant may be determined experimentally or estimated. A simple approach to estimating H_i is by using the saturation vapor pressure and solubility data (Lyman et al., 1990; Reid et al., 1987):

$$H_i = P_{vp} / S \tag{4-6}$$

where P_{vp} is the saturation vapor pressure (e.g., Pa) and S is the chemical solubility in water (e.g., mol/m^3). This expression is valid only for solutes for which the activity coefficient is constant at concentrations ranging from the solubility limit and below.

Since B(a)P is not volatile and it has a very low water solubility, its Henry's Law constant is very low. Table 4-6 presents reported Henry's Law constants for B(a)P which range from 4.9×10^{-2} $Pa \cdot m^3/mol$ to 1.6×10^{-1} $Pa \cdot m^3/mol$.

Southworth (1979) conducted experiments to determine the Henry's Law constant for six PAHs. The reported value for B(a)P was $< 1 \times 10^{-4}$ (or 2.47×10^{-1} $Pa \cdot m^3/mol$). Cohen et al. (1984) estimated the dimensionless Henry's Law for B(a)P from a correlation of H' values (i.e., $H' = H/RT$ in which R is the universal gas constant and T is the absolute temperature) versus molecular weight for several PAHs. Accordingly, the correlation shown in Figure 4.1 is given by the following equation:

Table 4-6. Henry's Law Constant (H) for Benzo(a)pyrene*

Henry's Law Constant (Pa· m³/mol)	Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	References	Source Cited
2.47×10^{-1}(a)	$<1\times10^{-4}$	unitless	NR	25°C	Experimental	Southworth, 1979(1)	
2.54×10^{-1}(a)	1.03×10^{-4}	unitless	NR	25°C	Calculated/ extrapolation	Cohen et al., 1984(1)	Southworth, 1979(1)
4.9×10^{-2}(b)	4.9×10^{-7}	atm-m³/mol	NR	25°C	Calculated	U.S. PHS, 1990(1)	U.S. EPA, 1982(1)
1.57×10^{-1}(b)	1.55×10^{-6}	atm-m³/mol	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	U.S. EPA, 1986(1)

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Conversion from reported value: **dimensionless H** $\times \dfrac{0.08205\ \text{l-atm}}{\text{mol K}} \times 298\ \text{K} \times \dfrac{1\ \text{m}^3}{1000\ \text{l}} \times \dfrac{101000\ \text{Pa}}{\text{atm}} = \text{Pa m}^3/\text{mol}$

(b) Conversion from reported value: **atm m³/mol** $\times \dfrac{101000\ \text{Pa}}{1\ \text{atm}} = \text{Pa m}^3/\text{mol}$

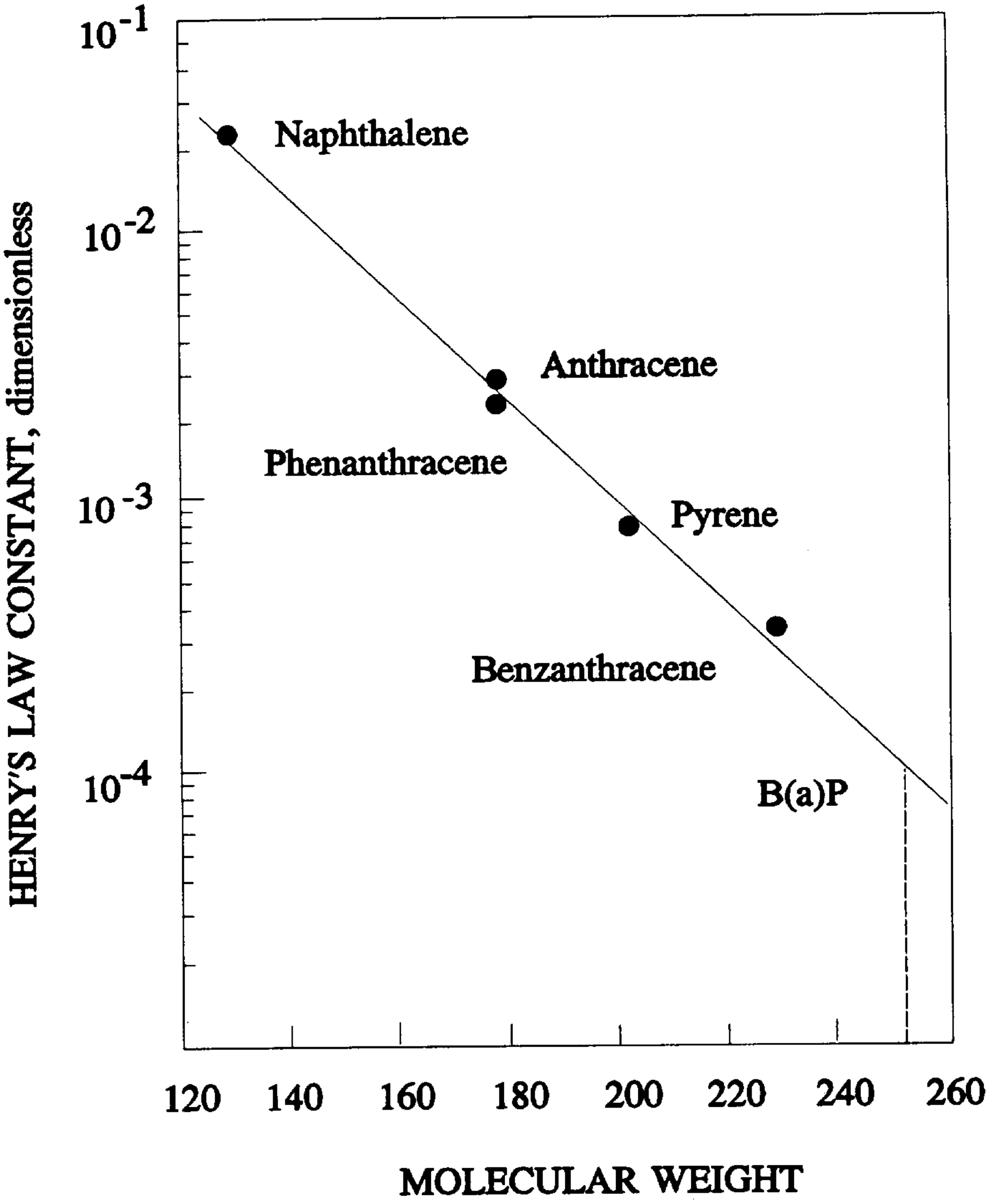

Figure 4.1. Correlation Between Henry's Law Constant and Molecular Weight (Cohen et al., 1984)

$$\log (H') = -0.01869\ (MW) + 0.7269 \qquad (4\text{-}7)$$

Thus, with a MW = 252.32 for B(a)P, the Henry's Law for B(a)P was calculated to be 1.03×10^{-4} (or 2.54×10^{-1} Pa m^3/mol), which is close to the value reported by Southworth (1979).

4.2.2 Octanol-Water Partition Coefficient

The dimensionless octanol-water partition coefficient, K_{ow}, is defined as the equilibrium ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system by the following equation:

$$K_{ow} = C_o/C_w \qquad (4\text{-}8)$$

where C_o is the concentration in octanol phase and C_w is the concentration in aqueous phase. When the concentrations of C_o and C_w are in the same units (e.g., mol/cm^3).

K_{ow} is an important parameter used in the assessment of environmental fate and transport for organic chemicals because the octanol phase is a surrogate for the lipid phase or organic carbon content of environmental compartments. K_{ow} for hydrophobic compounds such as B(a)P is considered as one of the most important physicochemical characteristic related to sorption on soils and sediments and bioaccumulation. Since K_{ow} has been correlated with water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life (Lyman et al., 1990), it is a key variable used in the estimation of these properties. Although K_{ow} is expected to vary with temperature, its temperature dependence is rarely reported in the literature.

Table 4-7 presents reported log K_{ow} values for B(a)P which range from 4.047 to 6.57. Although K_{ow} is expected to vary with temperature, its temperature dependence is rarely reported.

Table 4-7. Octanol-Water Partition Coefficient[1] (K_{ow}) for Benzo(a)pyrene*

log K_{ow}	Reported Uncertainty	Temperature	Technique	References	Source Cited
5.99	±0.08	23°C	Experimental°	Montgomery and Welkom, 1990(1)	Mallon and Harrison, 1984(1)
6.00	±0.1	23°C	Experimental†	Mallon and Harrison, 1984(1)	
6.5	NR	90-150°C‡	Experimental□	Montgomery and Welkom, 1990(1); Landrum et al., 1984(1)	Bruggeman et al., 1982(1)
5.81	NR	25±1°C	Calculated◆	Montgomery and Welkom, 1990(1); Mallon and Harrison, 1984(1)	Zepp and Schlotzhauer, 1979(1)
6.87	NR	25°C	Calculated◊	Yalkowsky and Valvani, 1979(5)	
6.57	NR	25°C	Calculated■	Mackay et al., 1980(5)	
6.06	NR	NR	Calculated++	U.S. PHS, 1990(1)	U.S. EPA, 1982(1)
5.98	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	Mackay and Paterson 1991; Miller et al., 1985(1)
6.04	NR	NR	NR	Montgomery and Welkom, 1990(1)	U.S. EPA, 1976(1)
4.047	NR	NR	NR	Lu et al., 1977(1)	

NR = Not Reported.

[1] Octanol-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase in a two-phase octanol/water system. Values for K_{ow} are thus dimensionless.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

○ Measured using high performance liquid chromatography (HPLC).

† Measured using UV spectroscopy.

□ Measured using reverse-phase thin-layer chromatography.

‡ These are the isothermal operating temperatures of the gas chromatograph in the experiment.

◆ Calculated from the correlation $K_p = 0.63\ F_f\ F_{oc}\ P$

◊ Calculated from the correlation

$$\log K_{ow} = -\frac{1}{0.88} \log S_w^c - \frac{0.01}{0.88}(T_{mp}) - \frac{0.012}{0.88}$$

■ Calculated from the correlation $\ln K_{ow} = 7.494 - \ln C' + 6.79\ (1 - T_{MP}/T)$

++ Calculated using FRAGMENT (based on Structure-Activity Relationship, SAR) calculation procedure (U.S. EPA, 1982).

Mallon and Harrison (1984) measured the octanol-water coefficient for B(a)P. Octanol and water phases that were equilibrated with respect to B(a)P were analyzed by both UV spectrophotometer and high-performance liquid chromatography (HPLC). The average measured values of log K_{ow} for B(a)P using the UV analysis was 6.00±0.1. Measurements using HPLC analysis generated an average value of log K_{ow} to be 5.99±0.08.

According to Mackay and Shiu (1977), existing correlations for log K_{ow} may be inaccurate for compounds of high molecular weight and low solubility. These estimation techniques, however, seem to give an upper bound to the calculated values of K_{ow}.

An experimental technique which seems to provide an excellent approximation of log K_{ow} was studied in detail by Landrum et al. (1984). This technique of reverse-phase thin-layer chromatography separation was first developed by Bruggeman et al. (1982) which correlates the retention parameter, R_m, with log K_{ow} by linear regression:

$$\log K_{ow} = 4.52 R_m + 4.81 \tag{4-9}$$

For B(a)P, R_m was determined to be 0.38 and thus, log $K_{ow} = 6.5$. This approximation of log K_{ow} is dependent on the retention parameter which is different for each column. Landrum et al. (1984) investigated pollutant binding to humic materials and dissolved organic carbon in water using reverse-phase separation. This approach is based on the assumption that the contaminants associated with humic materials in water will pass through the column while the unassociated hydrophobic contaminants will be retained by the column. The experiment was conducted using radiolabeling techniques. The log K_{ow} reported for B(a)P is 5.95.

Based on the correlation proposed by Yalkowsky and Valvani (1979), log K_{ow} can also be expressed as:

$$\log K_{ow} = -\frac{1}{0.88} \log S_w^c - \frac{0.01}{0.88}(T_{mp}) - \frac{0.012}{0.88} \tag{4-10}$$

where S^c_w is the aqueous solubility of a crystal (mol/L) and T_{MP} is the melting point in °C. This correlation was developed for indan and 31 different aromatic hydrocarbons.

Mackay et al. (1980) developed a correlation relating K_{ow}, aqueous solubility and melting point temperature for 56 organic compounds. They found that the correlation is satisfactory for 45 of the compounds including B(a)P. However, the correlation is less satisfactory for those compounds with a molecular weight of higher than 290. The correlation is given as:

$$\ln K_{ow} = 7.494 - \ln C^s + 6.79\,(1 - T_{MP}/T) \tag{4-11}$$

where C^s is the aqueous solubility in mol/m³, T is temperature (K), and T_{MP} is the melting point temperature (K).

For B(a)P, Eqs. 4-10 and 4-11 result in a log K_{ow} value of 6.87 and 6.57, respectively, given $C^s = 1.5 \times 10^{-5}$ mol/m³, $T_{mp} = 449.5$K, and T = 298K.

4.2.3 Vapor Phase/Particle Partitioning

Vapor/particle partitioning of B(a)P in the atmosphere is controlled by its vapor pressure and the total suspended particle (TSP) concentration. Semivolatile organic compounds (SOC), such as B(a)P, bound to atmospheric particles appear to consist of both a nonexchangeable fraction, which is strongly adsorbed to active sites or embedded within the particle matrix and is not in equilibrium with its vapor phase, and an exchangeable fraction, which is more loosely attached and is controlled by the concentration of SOC vapors in air (Bidleman, 1988). Junge (1977) presented a model of exchangeable SOC adsorption to aerosols. The adsorbed fraction (ϕ), solute saturation vapor pressure (p°, mm Hg) and total surface area of aerosols (S_T, cm²/cm³ air) were related through:

$$\phi = cS_T/(p^\circ + cS_T) \tag{4-12}$$

Junge (1977) assumed that $c = 1.7 \times 10^{-4}$ atm-cm and did not vary among compounds. This equation and other treatments of adsorption to aerosols have been reviewed by Pankow (1987), Bidleman and Foreman (1987) and Bidleman (1988). It is important to note that the Junge correlation only quantifies the exchangeable fraction of SOC between the particle and gas phase; however, the effect of nonexchangeable material can be significant for some organics including B(a)P (Pankow, 1988). Therefore, if the chosen chemical has significant nonexchangeable fraction, experimental values for partitioning should be utilized. At present, however, the available experimental data are insufficient to ascertain the extent of any nonexchangeable fraction of particle-bound B(a)P. Bidleman (1988) has estimated the percentage of B(a)P in the particulate phase in urban and background air to be approximately 95%, with 5% of B(a)P in the gas phase. It is also worth noting that in one of the early studies on B(a)P, Mukai et al. (1964) verified that the B(a)P emitted due to combustion is primarily in the particulate form.

4.2.4 Soil/Water-Organic Carbon Coefficient

The organic carbon partition coefficient (K_{oc}) is a measure of the tendency for organics to adsorb onto the soil (or sediment) and is defined as the ratio of the amount (mass) of a chemical adsorbed per unit mass of organic carbon in the soil (or sediment) to the concentration of the chemical in the soil (or sediment) solution at equilibrium,

$$K_{oc} = \frac{\text{(mg chemical adsorbed/kg organic carbon)}}{\text{(mg chemical dissolved/}\ell\text{ of solution)}} \tag{4-13}$$

The available methods for estimating K_{oc} involve empirical relationships with other properties of a chemical such as solubility, octanol-water partition coefficient, or bioconcentration factor for aquatic life. A convenient K_{oc} - K_{ow} correlation was proposed by Karickhoff et al. (1979) and K_{oc} - solubility correlations were proposed by Chiou et al. (1979) and Means et al. (1980). It is important to note that these correlations were derived for polycyclic aromatics and chlorinated hydrocarbons; however, B(a)P was not included as one of the study chemicals. The correlations are as follows:

$\log K_{oc} = 1.00 \log K_{ow} - 0.21$ (Karickhoff et al., 1979) (4-14)

$\log K_{oc} = 4.040 (\pm 0.038) - 0.557 (\pm 0.012) \log S$ (Chiou et al., 1979) (4-15)

where S is the aqueous solubility (μmol/L).

$\log K_{oc} = -0.82 \log S + 4.070$ (Means et al., 1980) (4-16)

where S is the aqueous solubility (μg/ml).

The values for log K_{oc} reported in the literature, based on different correlations, are given in Table 4-8. The reported K_{oc} values are in the range of 5.06 to 6.74. The differences in measured values can be attributed to the strong dependence of K_{oc} on soil characteristics such as pore size distribution, moisture content, pH, and soil chemistries. The variability of the estimated K_{oc} values is attributed to the use of different estimation equations as previously described, as well as the range of reported K_{ow} values.

4.2.5 Bioconcentration Factors

The traditional measure of a chemical's potential to accumulate in an organism is the bioconcentration factor (BCF), which is defined as a chemical concentration in an organism or tissue, on a net weight basis, divided by its concentration in the medium through which exposure occurs by direct contact (e.g., water for aquatic organisms, or air for terrestrial organisms). The concept of BCF addresses partitioning of a chemical into an organism by non-food routes. Specifically, BCF is defined as:

$$BCF = \frac{\text{(equilibrium concentration of chemical in receptor)}}{\begin{array}{c}\text{(average concentration of chemical in the medium}\\ \text{through which exposure occurs by direct contact)}\end{array}} \qquad (4\text{-}17)$$

It is convenient to use the same units for both the numerator and denominator which results in a dimensionless BCF. The term BCF is used with the assumption that uptake across external membranes from the media with which the receptor is in direct contact is

Table 4-8. Soil/Water-Organic Carbon Partition Coefficient (K_{oc})[1] for Benzo(a)pyrene*

log K_{oc}	Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	References	Source Cited
5.60 - 6.29	5.60 - 6.29	NR	NR	25±1°C	Calculated†	Montgomery and Welkom, 1990(1)	Karickhoff et al., 1979
5.77(a)	NR	NR	NR	25±1°C	Calculated†	Karickhoff et al., 1979	
5.78(b)	NR	NR	±0.08	25±1°C	Calculated†	Karickhoff et al., 1979	
5.83(c)	NR	NR	NR	25±1°C	Calculated†	Karickhoff et al., 1979	
6.29(d)	NR	NR	NR	25±1°C	Calculated†	Karickhoff et al., 1979	
5.6(e)	NR	NR	NR	25±1°C	Calculated†	Karickhoff et al., 1979	
6.36(f)	NR	NR	NR	25±1°C	Calculated†	Karickhoff et al., 1979	
3.837(g)	NR	NR	NR	25±1°C	Calculated†	Karickhoff et al., 1979	
5.06	NR	NR	±0.06	20°C	Calculated‡	Chiou et al., 1979	
6.05	NR	NR	NR	25°C	Calculated°	Means et al., 1980	
6.74	5.5×10^6	NR	NR	NR	Calculated◆	U.S. PHS, 1990(1)	U.S. EPA, 1982(1)

NR = Not Reported.

[1] Soil/water-organic carbon partition coefficient (K_{oc}) is defined as the ratio of the mass of a chemical adsorbed per unit mass of organic carbon in the soil or sediment to the concentration of the chemical in the solution at equilibrium.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

† Calculated from the correlation $\log K_{oc} = 1.00 \log K_{ow} - 0.21$

‡ Calculated from the correlation $\log K_{oc} = 4.040\ (\pm0.038) - 0.557\ (\pm0.012) \log S$; $S = 1.5\times10^{-2}$ µmol/L (Mackay and Shiu, 1977)

o Calculated from the correlation $\log K_{oc} = -0.82 \log S + 4.070$; $S = 0.0038$ µg/ml (Mackay and Shiu, 1977)

◆ Calculated from the correlation $K_{oc} = 0.48\ K_{ow}$; $K_{ow} = 1.15\times10^6$ (U.S. EPA, 1982)

(a) $\log K_{ow} = 5.98$ (Miller et al., 1985)

(b) $\log K_{ow} = 5.99$ (Mallon and Harrison, 1984)

(c) $\log K_{ow} = 6.04$ (U.S. EPA, 1976)

(d) $\log K_{ow} = 6.50$ (Landrum et al., 1984; Bruggeman et al., 1982; Yalkowsky et al., 1979)

(e) $\log K_{ow} = 5.81$ (Zepp and Schlotzhauer, 1979)

(f) $\log K_{ow} = 6.57$ (Mackay et al., 1980)

(g) $\log K_{ow} = 4.047$ (Lu et al., 1977) the chief pathway for chemical uptake by the organism. It is important to note that BCF values are compound-specific, medium-specific, and species-specific, and experimental data should be used whenever possible. In the absence of measured data, various empirical correlations may be utilized to estimate BCF values. BCF is frequently correlated with the K_{ow} or solubility (S) through correlations of the following form (Lyman et al., 1990):

$$\log(\mathrm{BCF}) = A + B \log(K_{ow}) \tag{4-18}$$

or

$$\log(\mathrm{BCF}) = C + D \log(S) \tag{4-19}$$

where A, B, C, and D are empirical constants. For example, Veith et al. (1980) derived the following values A = -0.23 and B = 0.76 for Eq. 4-18 based on a wide range of chemical classes and applicable for fish BCF. Kenaga and Goring (1980) derived values of C = 2,791 and D = -0.564, also based on a wide range of chemical classes, for use in Eq. 4-19 for fish BCF.

Recently, Banerjee and Baughman (1991) suggested the following fish BCF correlation for high MW organics which is applicable for compounds with high K_{ow} values

$$\begin{aligned} \log(\mathrm{BCF}) = {} & -1.13 + 1.02 \log(K_{ow}) + 0.84 \log(S_{octanol}) \\ & + 0.0004\,(T_{MP} - 25); \quad (r = 0.95) \end{aligned} \tag{4-20}$$

where $S_{octanol}$ is the molar solubility of the chemical in octanol (mol/L) and T_{MP} is the melting point in °C.

Table 4-9 shows BCFs for fish and other aquatic organisms. Differences among estimated values of BCF are attributed, in part, to the use of the different organisms utilized in developing the different correlations as shown above and the variability in the values for solubility and K_{ow} values that were used in those correlations.

Table 4-9. Bioconcentration Factor (BCF)[1] for Benzo(a)pyrene in Aquatic Organisms and Vegetation*

BCF	Reported Value	Reported Uncertainty	Temperature	Technique	References	Source Cited
Water/mosquito BCF	37	NR	NR	Experimental	Lu et al., 1977(1)	
Water/snail BCF	2177	NR	NR	Experimental	Lu et al., 1977(1)	
Water/Atlantic Salmon BCF	2310	NR	6.2°C	Experimental	Johnsen et al., 1989(1)	
Water/Atlantic Salmon BCF with aquatic humic substances	1160	NR	6.2°C	Experimental	Johnsen et al., 1989(1)	
Water/fish BCF	1110	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	
Soil/vegetation	0.013	NR	NR	Calculated†	Travis and Arms, 1988(1)	
Soil/root BCF	5.6×10^{-2}	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	Edwards, 1983(1)

NR = Not Reported.

[1] The bioconcentration factor (BCF) is the ratio of the concentration of a chemical in an organism to the concentration in water.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

† Calculated from the correlation $\log B_v = 1.588 - 0.578 \log K_{ow}$; $\log K_{ow} = 5.99$ (Mallon and Harrison, 1984).

Bioconcentration in Vegetation

The accumulation of B(a)P in vegetation is a complex process that can involve atmospheric deposition and root uptake. B(a)P is expected to sorb onto particulate matter in the atmosphere (Miguel and Friedlander, 1978) so the contamination of plants by direct dry and wet deposition of particle-bound B(a)P is a possible pathway for the uptake of B(a)P by vegetation. B(a)P present in the vapor phase can also be absorbed via the air-leaf pathway. Pollutants can also accumulate in vegetation through the uptake of water from contaminated soil. However, B(a)P is not very soluble in water, and thus, root uptake is not expected to be a major source of B(a)P uptake by vegetation.

The concentration of contaminants, due to root uptake, in vegetation can be expressed using a dimensionless plant-soil bioconcentration factor of the following form

$$B_{vd} = \frac{\text{concentration of chemical in plant}}{\text{concentration of chemical in soil}} = \frac{C_{vr}}{C_s} \qquad (4\text{-}21)$$

Travis and Arms (1988) derived a correlation for the above-ground portion of plants bioconcentration factor on a dry plant mass basis (B_{vd}) and K_{ow} based on data for 29 organic chemicals, including B(a)P. The equation is as follows:

$$\log B_{vd} = 1.588 - 0.578 \log K_{ow} \quad (r^2 = 0.525) \qquad (4\text{-}22)$$

From Eq. 4-22, B_{vd} for B(a)P is calculated to be 0.013 using a log K_{ow} of 5.99 (Mallon and Harrison, 1984).

Root Bioconcentration Factor

Briggs et al. (1982) proposed the following definition for the root bioconcentration factors for root crops:

$$B_{vw} = \frac{C_{veg}}{C_{soil}} \tag{4-23}$$

in which C_{veg} is the chemical concentration in the wet plant (i.e., ng chemical/kg soil). Thus, B_{vw} is related to B_{vd}, the root bioconcentration on a dry basis, by

$$B_{vw} = B_{vd} \times f_{dw} \tag{4-24}$$

where f_{dw} is the fraction of dry plant matter in the wet plant. Briggs et al. (1982) proposed the following correlation for B_{vw} applicable to hydrophobic organic compounds:

$$B_{vw} = \frac{0.82 + 0.028\, K_{ow}^{0.77}}{K_d} \tag{4-25}$$

in which $K_d = K_{oc}\, \chi$ where χ represents the mass fraction of the natural organic carbon in the soil. It is emphasized that B(a)P was not included in the development of the above correlation. Finally, it is noted that Edwards (1983) (cited by Hattemer-Frey and Travis, 1991) reported a soil-plant (via root pathway) BCF of 5.6×10^{-2} for B(a)P.

Air-to-Leaf Bioconcentration Factor

The basis for a vapor-phase bioconcentration factor for various airborne contaminants, from the atmosphere to vegetation was developed by Bacci et al. (1990). The dimensionless air-to-leaf bioconcentration factor can be expressed as

$$B_{vaw} = \frac{C_{va}\rho_p}{C_a F_v} \tag{4-26}$$

where C_{va} is the chemical concentration in the plant on a fresh (i.e., wet) plant mass basis (mg/kg), C_a is the concentration of a chemical in the air (mg/m^3), F_v represents the fraction of the chemical in the vapor phase, ρ_p is the density of the fresh plant (e.g., kg/m^3), and B_{vaw} represents the air-to-leaf bioconcentration factor on a dry plant mass basis. It has been suggested that B_{vaw} can be correlated with the chemical's water-air and octanol-water partition coefficients and the leaf properties (Bacci et al., 1990).

No measured or estimated values of air-to-leaf bioconcentration factors were found for B(a)P. Although B_{vaw} has not been measured for B(a)P, there are the air-to-leaf bioconcentration correlations for gaseous B(a)P that have been proposed in the literature

$$B_{vaw} = 0.19 + 0.7/H_i' + 0.05\ K_{ow}/H_i' \qquad \text{(Paterson and Mackay, 1991)} \qquad (4\text{-}27)$$

$$B_{vaw} = 0.022\ K_{ow}\ /\ H_i' \qquad \text{(Bacci et al., 1990)} \qquad (4\text{-}28)$$

where B_{vaw} is the air-to-leaf bioconcentration factor based (i.e., B_{va}) on wet mass, K_{ow} is octanol/water partition coefficient as previously defined, and H_i' is the dimensionless Henry's Law constant defined as $H_i' = H_i/RT$ (T is the temperature in K and R is the gas constant). Using, for example, K_{ow} value of 9.8×10^5 (Mallon and Harrison, 1984) and H_i' value of 1.03×10^{-4} (Cohen et al., 1984), a range of 2.1×10^8 to 4.7×10^8 was obtained for B_{vaw} from Eqs. 4-27 and 4-28. These values indicate that, for the portion of B(a)P present in the vapor phase, air-to-leaf transfer can be a significant pathway for bioconcentration in vegetation. However, it must be noted that 1,2,3,4-TCDD (not B(a)P) was used as the study chemical in the development of the above correlations. Thus, the above estimates of B_{vaw} values for B(a)P should only be regarded as indicative of the likely order of magnitude of B_{vaw} for gaseous B(a)P. Finally, it is noted that B_{va} on a dry plant basis is related to B_{vaw}.

$$B_{va} = B_{vaw} \times f_{dw} \qquad (4\text{-}29)$$

Accumulation Due to Dry Deposition of Particle-Bound B(a)P

Another process that can contribute to the above ground vegetation concentration of B(a)P is the dry deposition of particle-bound B(a)P onto plants. Only a portion of the chemical deposited is captured by the plant canopy and in general, as the particle size increases, there is less likelihood of initial retention (Witherspoon and Taylor, 1970; Markin, 1981). The fraction of the particles initially deposited and retained on the plants is quantified by the interception factor. The dry deposition velocity and the interception factor are needed for the estimation of the accumulation of B(a)P in vegetation due to deposition. The interception factor is affected by the leaf surface area and surface roughness, plant biomass, plant density, and other factors (Baes et al., 1984; Markin, 1981). Interception fractions related to dry matter yield of pasture and hay crops have been established for the major classes of feed crops and vegetables (Baes et al., 1984). Using the interception factor, the deposition flux intercepted by the plant canopy, N_p (e.g., $\mu g/m^2 \cdot day$), is given by

$$N_p = V_d \left(1 - e^{\beta M_p}\right) C_a^{(p)} \tag{4-30}$$

in which V_d is the particle deposition velocity (e.g., m/day) discussed in Section 4.3.3, β is foliar interception constant (m^2/kg of dry vegetation) and M_p is the plant dry mass inventory (kg/m^2), and $C_a^{(p)}$ is the concentration of the particle-bound chemical in the atmosphere (e.g., $\mu g/m^3$). A simple mass balance on a plant, assuming constant plant mass, chemical input due to dry deposition and chemical loss due to weathering results in the following equation for the chemical concentration in the plant, C_p (e.g., $\mu g/kg$ dry plant matter)

$$C_p = \frac{N_p}{M_p k_p} \left(1 - e^{-k_p t}\right) \tag{4-31}$$

in which k_p is a first-order weathering constant (e.g., 1/yr), and t is the time during which dry deposition is being considered. A 14-day half-life (i.e., $\tau_{1/2} = \ln 2/k_p$) is commonly used for particulate loss by weathering processes. It is interesting to note that half-lives measured in field studies range from about 2 to 34 days with a median of 10 days (Baes et al., 1984). Finally, values for the foliar interception constant can be estimated from Baes et al. (1984).

Accumulation Due to Wet Deposition

Wet deposition as described in Section 4.3.3.2 can also be an important process that contributes to accumulation of B(a)P in the above ground vegetation. However, no measured data on B(a)P accumulation in plants, due to wet deposition were found in the literature. In order to predict the concentration of B(a)P in plants, due to intermittent wet deposition, one must first perform a mass balance for B(a)P transported to the surface in rainwater, and secondly, one must be able to reasonably determine the fraction of B(a)P in precipitation that is captured by the plant canopy. Given the variability in the types of plants, their physiology and their complex interaction with the surrounding environment, it is apparent that the determination of B(a)P accumulation in vegetation due to wet deposition is difficult. However, it may be feasible to develop a simple model to determine an upper-bound estimate of the contribution of wet deposition to the accumulation of B(a)P by plants. For example, by using the "washout" ratio (Section 4.3.3.2), one can estimate the concentration of B(a)P in precipitation. Thus, a simple mass balance on a plant during a given rain event, assuming no degradation of B(a)P during rain, leads to an upper-limit estimate of the contribution of rain to the chemical concentration in the plant, $C_p^{(w)}$ (ng/kg fresh plant matter)

$$C_p^{(w)} = \Lambda_p^* C_a^{(p)} V_w / M_p \tag{4-32}$$

in which Λ_p^* is the washout ratio described in Section 4.3.3.2, $C_a^{(p)}$ is the atmospheric concentration of the particle-bound chemical, M_p is the mass of the fresh plant, and V_w is the volume of rainwater intercepted by the plant canopy for a given rain event.

4.2.6 Biotransfer Factors in Milk, Beef, and Eggs

The biotransfer factor (B_{TF}) concept addresses chemical accumulation in the receptor through food uptake. It has been suggested in the literature that the biotransfer factor (B_{TF}) may be more useful than BCFs in addressing exposure via food uptake since chemical exposure to feedstock animals may occur through both food and water pathways (Travis and Arms, 1988).

At steady state, the pathway specific biotransfer factor, B_{TFi}, for pathway i, can be expressed as

$$B_{TFi} = C_j / L_i C_{in} \tag{4-33}$$

and the overall biotransfer factor can be expressed as (Cohen, 1989)

$$B_{TF} = C_j \Big/ \left(\sum_{l=1}^{N} L_l C_{in} \right) = \left[\sum_{l=1}^{N} (Ex_k H_{kj}) + K_j V_j \right]^{-1} \tag{4-34}$$

V_j is the volume of the receptor and C_j and C_{in} are the concentrations of the contaminant in the receptor (or target organ) and the media associated with the receptor route. L_i represents the intake rate and Ex_k is the outflow (or elimination) stream associated with the particular elimination pathway k. H_{kj} is the partition coefficient between receptor j and outflow stream k. The overall biochemical transformation of a given contaminant is described by first order reaction kinetics with a rate constant K_j. Using Eq. 4-34, for example, one can define a B_{TF} for the concentration of a contaminant in cow's milk where $\Sigma L_i C_{in}$ is the total contaminant intake during feeding, water drinking, and inhalation. In general, the B_{TF} is not constant since V_j, the volume of the receptor, may vary with time, and the partition coefficient, H_{kj}, and the reaction rate constant, K_j, are likely to be a function of the activity of the receptor. Thus, one is led to conclude that B_{TF} and B_{TFi} are likely to be time variant parameters. Despite this concern, the concept of biotransfer factors is rooted in environmental exposure assessment.

As previously noted, feedstock animals may be exposed to B(a)P through ingestion of contaminated feed crops and drinking water, as well as direct inhalation. Human exposure can subsequently result from ingestion of contaminated animal products. Assessing the magnitude of human exposure to a contaminant such as B(a)P from ingestion of animal products depends largely on the ability to predict the extent of its bioaccumulation in aquatic and terrestrial food chains. Biotransfer factors for organics in beef and milk have been correlated with the equilibrium octanol/water partition coefficient (Travis and Arms, 1988), although the concept of B_{TF} should be regarded as a transport parameter rather than simply a physicochemical property (Cohen, 1989). It is important to note that B_{TF} correlations determined by Travis and Arms (1988) are subject to uncertainties in the input data from which B_{TF} values were derived. For instance, McKone and Ryan (1989) noted that the uncertainty in the Travis and Arms (1988) correlations for 95% confidence interval for both the feed to milk biotransfer factor, B_m, and the feed to meat biotransfer factor, B_b, is approximately 2 orders of magnitude.

The biotransfer factors for milk (B_m) and meat (beef; B_b) have been defined by Travis and Arms (1988) as follows:

$$B_m = \frac{\text{(concentration in milk (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \qquad (4\text{-}35)$$

$$B_b = \frac{\text{(concentration in meat (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \qquad (4\text{-}36)$$

In general, measured concentration of organics in milk or meat fat are converted on a whole milk or fresh meat basis, assuming meat contains 25% fat and whole milk contains 3.68% fat.

As shown in Table 4-10, Travis and Arms (1988) derived a log K_{ow} vs. log B_m correlation based on data for 28 organic chemicals in milk (B(a)P was included) which yielded the following equation:

$$\log B_m = -8.056 + 0.992 \log K_{ow}, \quad r=0.74 \quad 2.81 < \log K_{ow} < 6.89 \qquad (4\text{-}37)$$

In the above equation, B_m was based on data for ingestion only and did not include contaminant uptake via inhalation or dermal absorption. Using Eq. 4-37 and a log (K_{ow}) value of 5.99 for B(a)P (Mallon and Harrison, 1984), one obtains log (B_m) = -2.11 (or $B_m = 7.69 \times 10^{-3}$).

Table 4-10. Biotransfer Factors (BTF) and Biomagnification Factors (BMF) for Benzo(a)pyrene*

Reported Value	Reported Units	Reported Uncertainty	Temperature	Technique	References	Source Cited
Feed to beef BTF 0.025	d/kg	NR	NR	Calculated†	Hattemer-Frey and Travis, 1991$^{(1)}$	Travis and Arms, 1988
Feed to milk BTF 7.69×10^{-3}	d/kg	NR	NR	Calculated‡	Hattemer-Frey and Travis, 1991$^{(1)}$	Travis and Arms, 1988
Fish BMF 930		NR	NR	Experimental	Lu et al., 1977$^{(1)}$	
Alga BMF 5,258		NR	NR	Experimental	Lu et al., 1977$^{(1)}$	
Mosquito BMF 11,536		NR	NR	Experimental	Lu et al., 1977$^{(1)}$	
Snail BMF 82,231		NR	NR	Experimental	Lu et al., 1977$^{(1)}$	
Daphnia BMF 134,248		NR	NR	Experimental	Lu et al., 1977$^{(1)}$	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

† Calculated using $\log B_m = -8.056 + 0.992 \log K_{ow}$, $\log K_{ow} = 5.99$ (Mallon and Harrison, 1984).

‡ Calculated using $\log B_b = -7.6 + \log K_{ow}$; $\log K_{ow} = 5.99$ (Mallon and Harrison, 1984).

Travis and Arms (1988) also derived the following correlation for B_b (see Eq. 4-36):

$$\log B_b = -7.6 + \log K_{ow} \qquad n = 36, r = 0.81 \qquad \text{(Travis and Arms, 1988)} \qquad (4\text{-}38)$$

which for B(a)P results in a B_b value of 0.025.

Experimentally determined or estimated biotransfer factors for feed-to-egg were not found in the literature for B(a)P. The CAPCOA guidelines, for example, assume that the biotransfer factor for eggs is the same as that for beef. Given the lack of data, this approximation may be acceptable for a screening-type analysis.

The measurement-specific definition of BCF and B_{TF} as discussed above must be distinguished from other terms used to describe the accumulation of a chemical concentration in an organism via the food chain. Such terms include biomagnification and bioaccumulation (Lyman et al., 1990). Biomagnification refers to a further increase in concentration attributable to uptake from food. Bioaccumulation is a broader term that indicates uptake from all sources and thus includes effects of both biomagnification and bioconcentration (Clark et al., 1988). These terms are associated with increasing concentrations along a food chain, which could result in higher concentrations factors in top-order consumers. Biomagnification factors for B(a)P were determined experimentally by Lu et al. (1977), in a laboratory ecosystem, for fish, alga, mosquito, snail, and daphnia. The values are reported in Table 4-10.

The overall bioaccumulation factor K_b can be shown to be related to the biotransfer factors, when exposure occurs in a single medium, by the following relation (Cohen, 1989)

$$K_b = C_j/C_i = B_{TF}(\sum_{i=1}^{N} L_i C_{in})/C_i \qquad (4\text{-}39)$$

where C_j is the concentration of the contaminant in the receptor, C_i is the concentration in the media most directly associated with the exposure route, B_{TF} is the biotransfer factor, L_i

is the intake rate and C_{in} is the concentration in either the feed, drinking water, inhaled air. It is important to note that bioaccumulation factors are a function of the receptor characteristics, the chemical type and temperature. The bioaccumulation factor is equivalent to the bioconcentration factor when the exposure takes place only via contact with a single medium without accumulation due to food consumption. The above approach assumes implicitly that K_b is time invariant. As discussed previously, for biota, K_b is often correlated with K_{ow} (Kenaga and Goring, 1980; Mackay et al., 1980; Veith and Rosian, 1983).

4.2.7 Bioavailability

The bioavailability of a chemical is defined as the fraction of a compound in a matrix that can be released from that matrix and consequently absorbed by an organism, and hence, is available to elicit a biological effect (SCAQMD, 1988). The release and uptake of a chemical constitute facets of bioavailability, although its biological effect is often used as a measure of bioavailability. Since risk is considered to be a function of both exposure and toxicity, bioavailability is an important consideration in determining potential risk from airborne contaminants (SCAQMD, 1988). Bioavailability is often considered when assessing dose from inhalation and ingestion pathways.

Johnsen et al. (1989) investigated the influence of natural aquatic humic substances on the bioavailability of B(a)P to Atlantic salmons. They concluded that the presence of humic substances reduced the bioavailability of B(a)P to living organisms. Oikari and Kukkonen (1990) measured the bioaccumulation of B(a)P in Daphnia magna using a wide range of natural occurring dissolved organic carbon (DOC) levels and their results suggested that the bioavailability of B(a)P decreases in waters with DOC consisting of a significant fraction of high-molecular weight hydrophobic acids. In another study, McElroy et al. (1989) demonstrated that PAH in oil are more bioavailable than PAH released through high temperature pyrolysis.

More recently, Kukkonen and Oikari (1992) isolated unchlorinated kraft lignin and chlorolignin from pulp mill effluents and studied their ability to bind B(a)P in water.

Bioconcentration factors of B(a)P for waterflies (Daphnia magna) from the aqueous systems that contained one of the above mentioned compounds were compared to that of a control aqueous system. It was found that the bioconcentration factors for the aqueous systems that contained unchlorinated kraft lignin and chlorolignin were significantly lower than that of the control systems indicating a lowering of the bioavailability of B(a)P to waterflies in the presence of pulp mill effluent components. In another recent study, Narbonne et al. (1992) studied the mussels' (Mytillus galloprovincialis) uptake of B(a)P adsorbed to sediment. The data indicate that only 15% of the B(a)P initially adsorbed onto the sediment dissolved in the water and 0.7% of the adsorbed B(a)P was partitioned to the mussels.

4.3 Intermedia Transport Parameters for B(a)P

The following subsections define the specific intermedia transport factors reviewed in this study along with the reported and estimated parameter values.

4.3.1 Diffusion Coefficients in Air and Water

Molecular diffusion is the net transport of a molecule within a single phase (e.g., liquid or gas) that results from intermolecular collisions rather than turbulence or bulk transport. Diffusion can result from pressure, temperature, and concentration gradients but under environmental conditions, only diffusion due to concentration gradient is considered. The diffusive flux due to concentration gradients is defined by Fick's Law as:

$$J_A = -D_{AB}\, dC_A/dx \tag{4-40a}$$

in which J_A is the diffusion flux for compound A (e.g., mg/m^2·s), dC_A/dx is the concentration gradient along the x direction and D_{AB} is the diffusion coefficient of A in medium B (e.g., units of cm^2/s). For example, for air/water exchange processes, molecular diffusion dominates chemical transport near the air/water interphase (in both the air and water phases). In general, the mass flux, N (e.g., mg/m^2·s), across an interface (between two phases) is expressed by an equation of the form

$$N = K\Delta C \qquad (4\text{-}40b)$$

in which ΔC is an appropriate concentration driving force and K is an appropriate mass transfer coefficient. Correlations of mass transfer coefficients include a dependence on the molecular diffusivity, which can be estimated as described below.

Diffusion coefficients in air can be calculated by using the correlation of Fuller et al. (1966).

$$D_{BA} = \frac{10^{-3}T^{1.75}\sqrt{M_r}}{P\,(V_A^{1/3}+V_B^{1/3})^2} \;,\; \mathrm{cm^2/s} \;,\quad \text{where } M_r = \frac{M_A+M_B}{M_A M_B} \qquad (4\text{-}41)$$

in which the subscripts B and A denote the solute (e.g., B(a)P) and air, respectively, T is temperature (K), M is molecular weight, P is the pressure (atm), and V_A and V_B are the molar volumes (cm^3/mol) for air and the solute in question (e.g., B(a)P), respectively.

The diffusivity in air can also be estimated from the correlation of Wilke and Lee (1955).

$$D_{BA} = \frac{B' T^{3/2}\sqrt{M_r}}{P\sigma_{AB}^2\,\Omega} \qquad (4\text{-}42)$$

where $B' = 0.00217 - 0.00050\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}$, $M_r = (M_A + M_B)/M_A M_B$, σ_{AB} is characteristic length of molecule A interacting with B, Å, M is molecular weight, T is temperature (K), P is pressure (atm), and Ω is collision integral (see Reid et al., 1987).

Correlations commonly used to calculate diffusion coefficients in water are given below.

Wilke and Chang (1955)

$$D_{BW} = \frac{7.4 \times 10^{-8}(\phi_W M_W)^{1/2}T}{\eta_W\, V_B^{0.6}} \;,\quad \mathrm{cm^2/s} \qquad (4\text{-}43)$$

where M_W is molecular weight of water (g/mol), T is temperature (K), η_W is viscosity of water (cP), V_B is molar volume of solute B (e.g., B(a)P) at its normal boiling temperature (cm^3/mol), and ϕ_W is the solvent association factor which equals 2.6 for water (Wilke and Chang, 1955).

Hayduk and Laudie (1974)

$$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14} \, V_B^{0.589}} \, , \quad cm^2/s \tag{4-44}$$

where η_W is viscosity of water (cP) (1 cP = 1 poise = 1 g/cm.s) and V_B is the solute molar volume (cm^3/mol).

Hayduk et al. (1982)

$$D_{BW} = 1.25 \times 10^{-8}(V_B^{-0.19} - 0.292)T^{1.52}\eta_W^{\epsilon^*} \, , \quad cm^2/s \tag{4-45}$$

where V_B is the solute molar volume (cm^3/mol), η_W is viscosity of water (cP), and $\epsilon^* = (9.58/V_B) - 1.12$.

Table 4-11 presents values for diffusion coefficients of B(a)P in air and water. No experimental values were found in the literature. The methods of Fuller et al. (1966), Wilke and Chang (1955), Hayduk and Laudie (1974), and Hayduk et al. (1982) were used to calculate B(a)P diffusion coefficients in air and water which are reported in Table 4-11.

4.3.2 Gaseous Mass Transfer Across the Air-Water Interface

The traditional approach to calculating the flux of a compound between air and water phases is to use the two-film theory in which it is assumed that the concentrations immediately on either side of the interface are in equilibrium as can be expressed by a Henry's Law constant (Lewis and Whitman, 1924). The flux, N, can be expressed as:

$$N = K_G (C_g - H'C_l) = K_L (C_l - C_g/H') \tag{4-46}$$

Table 4-11. Diffusion Coefficient in Air and Water for B(a)P*

Media	Diffusion Coefficient (cm²/s)	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
Air	0.049	7.6% (Absolute average error)	298	Estimated(a)	Section 4.3.1	Fuller et al., 1966
Water	5.984×10^{-6}	NR	298	Estimated(b)	Section 4.3.1	Wilke and Chang, 1955
Water	5.684×10^{-6}	5.8% (Absolute average error)	298	Estimated(c)	Section 4.3.1	Hayduk and Laudie, 1974
Water	4.487×10^{-6}	NR	298	Estimated(d)	Section 4.3.1	Hayduk et al., 1982

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Fuller et al. method, 1966.

$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P\,(V_A^{1/3} + V_B^{1/3})^2}\ , \quad \mathrm{cm^2/s}\ , \quad \text{where } M_r = \frac{M_A + M_B}{M_A M_B}$$

(all variables are defined in Section 4.3.1)

$P = 1$ atm
$T = 298$ K
$M_A = 28.97$ g/mol (Lyman et al., 1990)
$M_B = 252.32$ g/mol (Section 4.1.7)
$V_A = 20.1\ \mathrm{cm^3/mol}$ (Lyman et al., 1990)
$V_B = 263\ \mathrm{cm^3/mol}$ (Miller et al., 1985)

Table 4-11. Diffusion Coefficient in Air and Water for B(a)P
(Continued)

(b) Wilke and Chang (1955)

$$D_{BW} = \frac{7.4 \text{ x } 10^{-8}(\varnothing_W M_W)^{1/2}T}{\eta_W \; V_B^{0.6}} \quad , \quad cm^2/s$$

where ϕ_w = solvent association factor (ϕ_w = 2.6 for water)
M_w = molecular weight of water (i.e., 18 g/mol)
η_w = viscosity of water (at 298K, η_w = 0.8906 cP)
V_B = molar volume of B(a)P which is 263 cm^3/mol
T = temperature taken as 298K

(c) Hayduk and Laudie method, 1974.

$$D_{BW} = \frac{13.26x10^{-5}}{\eta_W^{1.14} \; V_B^{0.589}} \quad , \quad cm^2/s$$

where η_w is viscosity of water (cP), which is 0.8904 cP at 298K
V'_B is molar volume (cm^3/mol), which is 263 cm^3/mol for B(a)P.

(d) Hayduk et al. method, 1982.

$$D_{BW} = 1.25 \text{ x } 10^{-8}(V_B^{-0.19} - 0.292)T^{1.52}\eta_W^{\epsilon^*} \quad , \quad cm^2/s \quad ,$$

(all variables are defined in Section 4.3.1)

V_B = 263 cm^3/mol
T = 298 K
η_w = 0.8906 cP at 298K (Lyman et al., 1990)
ε^* = $(9.58/V_B)$ - 1.12

where K_G and K_L are the overall mass transfer coefficients (cm/s) for the gas and liquid phase, respectively, H' is a unitless Henry's Law constant, and C_g and C_l are concentrations in gas and liquid phase, respectively. The overall mass transfer coefficients for the gas and liquid phase can be defined as:

$$1/K_G = 1/k_g + H'/k_l \tag{4-47}$$

$$1/K_L = 1/k_l + 1/H'k_g \tag{4-48}$$

where k_g is a gas-phase mass transfer exchange coefficient (cm/s) and k_l is a liquid-phase mass transfer coefficient. The important parameters that are needed in order to predict N are H' (see Section 4.2.1) and the mass transfer coefficients k_g and k_l. The mass coefficients depend on the prevailing turbulence level (as determined by water currents and wind), on temperature, on properties of the solute such as diffusivity, or molecular size (Mackay and Yeun, 1983), and on the depth of the water body (Cohen, 1986). Thus, one must ensure that k_g and k_l are determined for the appropriate environmental conditions. Experimental studies of volatilization of organics in laboratory wind-wave tanks have demonstrated that $k_g \gg k_l$. In general, for chemicals for which k_l is of the same order of magnitude as $H'k_g$, both k_l and k_g should be considered as given in Eqs. 4-46 - 4-48. Predictive equations, appropriate for screening-level analysis, that can be used to estimate k_g and k_l are given in Sections 4.3.2.1 and 4.3.2.2.

4.3.2.1 Air/Water - Air Side - Mass Transfer Coefficient (k_g) for B(a)P

Numerous theories and empirical equations have been proposed to predict k_g. The theoretical expressions for k_g as proposed by Brutsaert (1975) are particularly useful for predicting k_g. For a rough surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^{+}\left(C_D^{-1/2} - 5\right) + 7.3\ Re_o^{0.25}\ Sc_a^{1/2}\right]^{-1}, \quad Re_o > 2 \tag{4-49}$$

and for a smooth surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^{+}\left(C_D^{-1/2}-13.5\right) + 13.6\ Sc_a^{2/3}\right]^{-1}, \quad Re_o < 0.13 \qquad (4\text{-}50)$$

in which the Schmidt number, Sc_a, is given by the ratio ν_a/D_a, where D_a is molecular diffusivity in air (Section 4.3.1), U_{10} is the wind speed at a reference height (usually 10 meters), C_D is the wind drag (or stress) coefficient, ϵ_D^{+} is the ratio of the eddy momentum diffusivity (ϵ_m) to the eddy mass diffusivity (ϵ_D), often approximated to be near unity, and Re_o is the roughness Reynolds number. Eqs. 4-49 and 4-50 are strictly applicable to a neutral atmospheric condition. However, as suggested by Brutsaert (1975), Eqs. 4-49 and 4-50 are probably still satisfactory even under very unstable, but apparently not under stable conditions. For non-neutral conditions, the mass flux equations Eq. 4-46 must be used with caution since the bulk gas phase concentration as used in Eq. 4-46 may lie outside the dynamic sublayer (Brutsaert, 1975). Under such conditions, a detailed air quality model which considers the concentration profile at the air-side must be considered. Thus, one should regard the use of the estimation methods for k_g as given in this section as suitable for neutral conditions and for screening-level analysis for non-neutral conditions. The prediction of k_g for non-neutral conditions can be accomplished using the approach as presented by Brutsaert (1975). However, it should be noted that within the context of screening-level analysis, as is the case in the CAPCOA model, the application of Eqs. 4-49 and 4-50 is sufficient especially for sparingly soluble hydrophobic organic compounds.

The use of Eqs. 4-49 and 4-50 requires the wind drag coefficient velocity as input. The wind-drag coefficient, C_D, is defined as (Wu, 1980)

$$C_D = \left(\frac{U_W^{*}}{U_{10}}\right)^2\left(\frac{\rho_W}{\rho_a}\right) = \left(\frac{U_a^{*}}{U_{10}}\right)^2 \qquad (4\text{-}51)$$

in which U_W^* is the surface shear velocity given by:

$$U_W^* = \sqrt{\frac{\tau_s}{\rho_w}} \tag{4-52}$$

where τ_s is the shear stress imparted by the wind on the water surface, ρ_w is the water density, ρ_a is the air density, and U_{10} is the wind speed measured at a reference height (usually 10m) above the water surface. It is noted that the water-side friction velocity U_w^* and U_a^* are related through the simple relation $\rho_a(U_a^*)^2 = \rho_w(U_w^*)^2$ which arises from the condition of stress equality at the air/water interface. Given wind speed profile data, one can estimate U^*_a using the following equation:

$$U_a^* = U_{10}\, k \left[\ln\left(\frac{z_{10}}{z_o}\right) - \psi_M \left(\frac{z}{L}\right) + \psi_M\left(\frac{z_o}{L}\right) \right]^{-1} \tag{4-53}$$

where k is the von Karman constant ($k = 0.4$), U_{10} is the velocity at the reference height, z_{10}, ψ_M is a stability function, and L is the Obukhov stability parameter (Holtslag and Van Ulden, 1983; and reference therein). It is noted that for neutral conditions the function ψ_M is set to zero. The roughness Reynolds number, Re_o, is defined by:

$$Re_o = U_a^*\, z_o/\nu_a \tag{4-54}$$

where z_o is the effective surface roughness height and ν_a is the kinematic viscosity of air. The effective surface roughness height can be estimated for smooth water surfaces as (Brutsaert, 1975)

$$z_o \approx 0.135(\nu_a/U^*_a) \quad , \quad \text{cm} \tag{4-55}$$

and for a rough surface,

$$z_o = a(U^*_a)^b \quad , \quad \text{cm} \tag{4-56}$$

in which U^*_a is the air-side friction velocity (cm/s) and ν_a is the kinematic viscosity (cm/s^2). The parameters a and b are given by $a = 1.69\times10^{-2}$ and $b = -1$ for $U^*_a \leq 6.89$ cm/s, and $a = 1.65\times10^{-4}$, $b = 1.4$ for $U^*_a > 6.89$ cm/s (Jirka and Brutsaert, 1984). An alternative correlation for z_o was proposed by Wu (1980) for a large water fetch in which z_o was expressed by:

$$z_o = 0.0144(U^*_a)^2/g, \quad (g=981,\ \mathrm{cm/s^2}) \qquad (4\text{-}57)$$

For a large water fetch, the wind-stress coefficient near neutral conditions can be estimated from (Cohen, 1983)

$$C_D = 8.5\times10^{-4} \ , \qquad U_{10} < 5\ \mathrm{m/s} \qquad (4\text{-}58)$$

$$C_D = [0.85 + 0.11\,(U_{10} - 5)]\times10^{-3} \ , \qquad 5\ \mathrm{m/s} \leq U_{10} \leq 20\ \mathrm{m/s} \qquad (4\text{-}59)$$

$$C_D = 2.5\times10^{-3} \ , \qquad U_{10} > 20\ \mathrm{m/s} \qquad (4\text{-}60)$$

or (Wu, 1980)

$$C_D = (0.8 + 0.065U_{10})\times10^{-3} \ , \qquad U_{10} \geq 1\ \mathrm{m/s} \qquad (4\text{-}61)$$

As an illustration of the above approach, the gas-side mass transfer coefficient as obtained from Eqs. 4-49, 4-50 (with linear interpolation in the region $0.13 \leq Re_o \leq 2$), and Eqs. 4-56 and 4-61 for z_o and C_D, respectively, for B(a)P at 20°C is given in Figure 4.2.

Other alternate expressions for k_g under neutral (or near-neutral) conditions have been proposed in the literature. For example, Lyman (1990) recommends the correlation of Southworth (1979) for k_g

$$k_g = 1137.5\,(V_{wind}+V_{curr})\sqrt{\frac{18}{MW}} \ , \qquad \mathrm{cm/hr} \qquad (4\text{-}62)$$

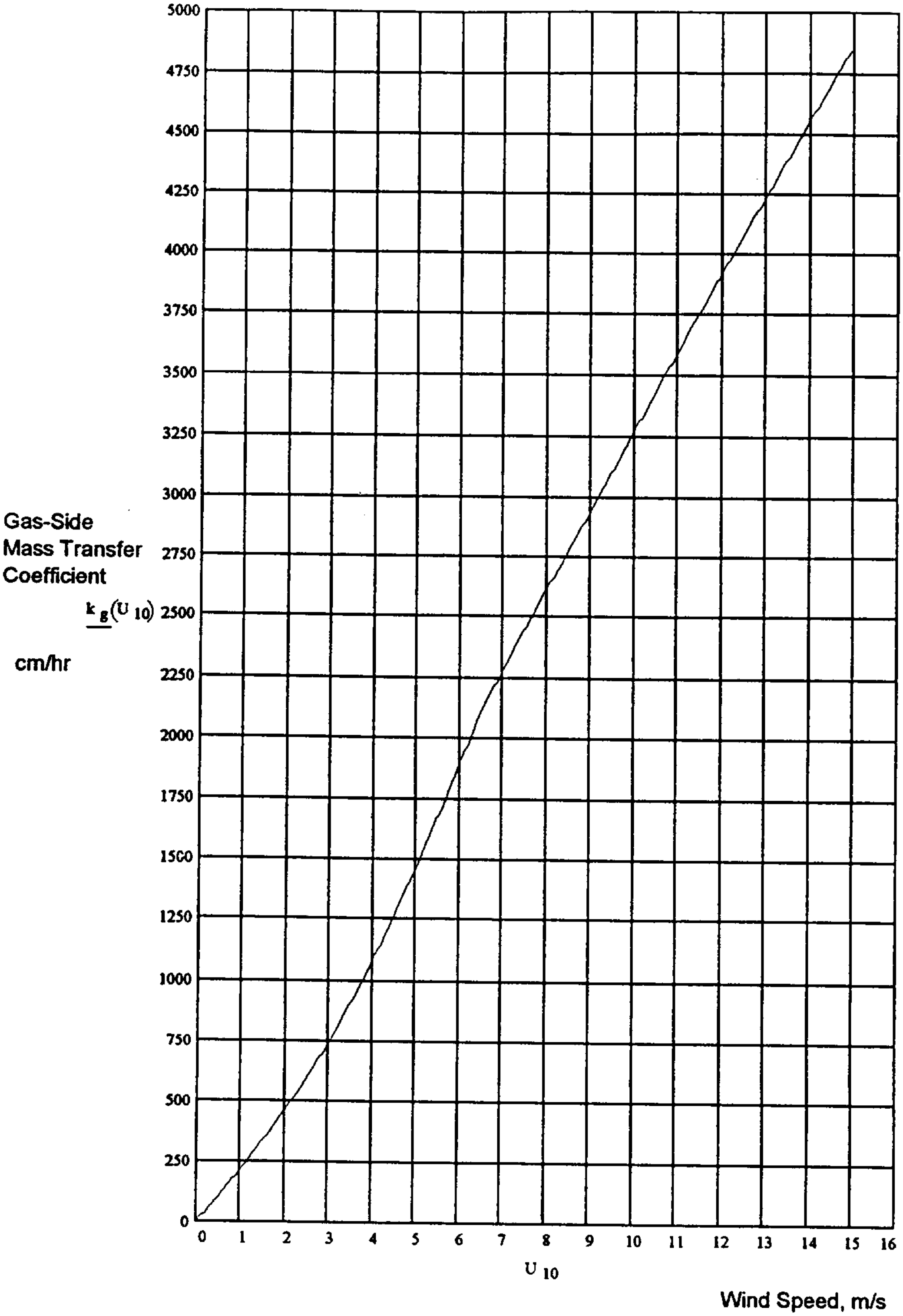

Figure 4.2 Gas-Side Mass Transfer Coefficient for Benzo(a)Pyrene at 20°C for Water/Air Mass Transfer at Large Fetch. (Based on the Correlation of Brustsaert, 1975).

where V_{wind} and V_{curr} are the velocities of the wind and water current, respectively (m/s), and MW is the molecular weight of the contaminant of interest. As an example, using V_{wind} = 3 m/s and V_{curr} = 1 m/s, k_g for B(a)P is estimated as 1215 cm/hr. It is important to note that the atmospheric stability condition for which Eq. 4-62 applies was not reported. Moreover, the theoretical basis of the Southworth (1979) equation is questionable because of the linear additivity of the wind and air currents in Eq. 4-62. The hydrodynamic effects of the wind relative to the water current on the roughness and velocity of the water surface are likely to be very different, as supported by later researchers (cited by Cohen, 1986) who have found that the effect of wind velocity and current velocity on k_g vary by different powers. Finally, a convenient correlation for k_g, determined based on laboratory measurements in a small wind-wave tank (fetch < 3m) under near neutral conditions, was proposed by Mackay and Yeun (1983).

$$\frac{k_g}{U_a^*} = 46.2 \times 10^{-3}\ Sc_a^{-0.67} \qquad (4\text{-}63)$$

Eq. 4-63 results in k_g values which are about 20%-40% higher than predicted by Eqs. 4-49 and 4-50. The higher prediction by the Mackay and Yeun (1983) correlation may be, in part, due to the difference in surface roughness condition in their short fetch wind-wave tank, for a given U_a^*, relative to the condition that would exist at long fetch.

4.3.2.2 Air/Water - Liquid Side - Mass Transfer Coefficient (k_l) for B(a)P

The water-side mass transfer coefficient, k_l, for large water bodies (i.e., reservoirs, lakes, oceans) can be estimated using the theoretical correlation of Cohen and Ryan (1985), which was found to be in excellent agreement with available data for a water-side friction velocity in the range of 0.5-6 cm/s,

$$k_l/U_w^* = a\ Sc_w^{-n} \qquad (4\text{-}64)$$

in which Sc_w is the Schmidt number given by the ratio ν_w/D_w where ν_w is the water kinematic viscosity and D_w is the chemical molecular mass diffusivity in water. The constants a and n are weak functions of the dimensionless water surface velocity U_s^+ ($U_s^+ = U_s/U_w^*$, in which U_s is the wind-induced surface water velocity), given by:

$$a = a_0 - a_1 \ln U_s^+ \qquad (4\text{-}65)$$
$$n = n_0 - n_1 \ln U_s^+$$

where

$$a_0 = 0.09691;\ a_1 = 0.01053;$$
$$n_0 = 0.5778;\ n_1 = 0.01771 \qquad (4\text{-}66)$$

For a long fetch (say ≥ 30m), the surface velocity is equal to about 3.5% of the wind speed (i.e., $U_s = 0.035\ U_{10}$), while for short fetch (say less than about 10m), $U_s \approx 0.020\ U_{10}$ (Wu, 1975; Plate and Friedrich, 1984). Eq. 4-64 was found to be in excellent agreement with laboratory data from wind-wave facilities with an average error of about 16 percent. As an illustration, the dependence of k_l on wind speed for B(a)P at 20°C is shown in Figure 4.3 where Eqs. 4-52 and 4-61 were used to determine U_w^*.

The prediction of k_l in flowing water bodies (e.g., rivers) requires consideration of the river current and the river depth (Cohen, 1986). There are numerous studies on the reaeration coefficient in flowing streams (O'Connor, 1983; Lyman et al., 1990), and the water-side mass transfer coefficient k_l can be estimated from the reaeration coefficient, k_v (e.g., hr^{-1}), by using the following relation:

$$k_l = \left(\frac{D}{D_o}\right)^{1/2} h\ k_v \qquad (4\text{-}67)$$

in which h is the depth of the water body (e.g., m), D is the mass diffusivity of the compound of interest (e.g., B(a)P), D_o is the mass diffusivity of at the temperature at which

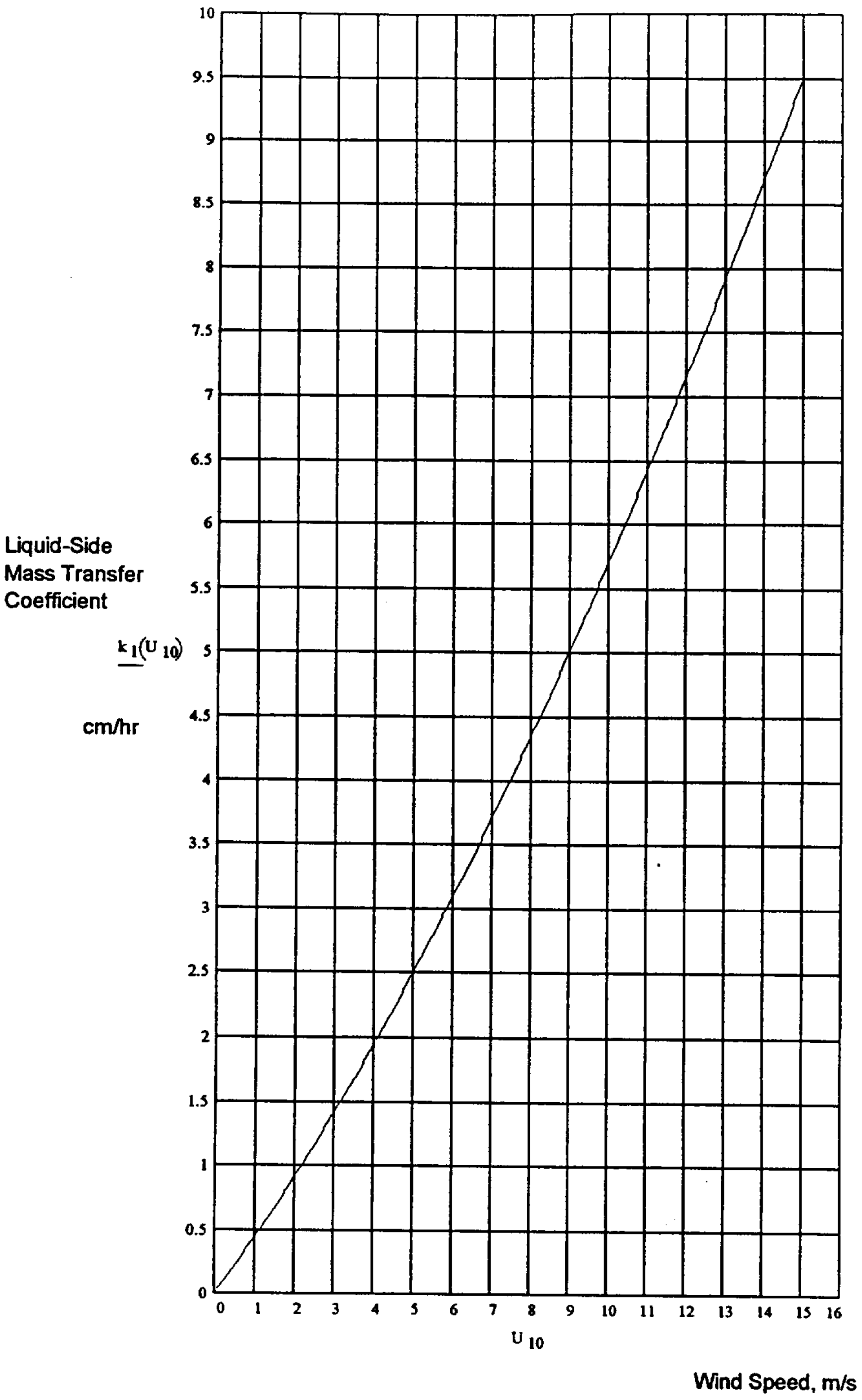

Figure 4.3 Liquid-Side Mass Transfer Coefficient for Benzo(a)Pyrene for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlation of Cohen and Ryan, 1985).

k_v is known and h is the river depth (Cohen, 1986). Lyman et al. (1982) recommended the following empirical correlations, which are based on field data, for predicting k_v:

$$k_v = 1.08\,(1 + 0.17\,F^2)\,(V_{curr}\,S)^{0.375}, \ \text{hr}^{-1} \tag{4-68}$$

$$k_v = 0.00102\,V_{curr}^{2.695}\,h^{-3.085}\,S^{-0.823}, \ \text{hr}^{-1} \tag{4-69}$$

$$k_v = 638\,V_{curr}\,S, \ \text{hr}^{-1} \tag{4-70}$$

in which S is the river bed slope (m drop/ m run), F is the dimensionless Froude number ($F = V_{curr}/gh$), and h is the river depth (m). The use of an average value of k_v determined from the above three equations was recommended by Lyman et al. (1982). Other relations for k_v that are suitable when bed slope information is not available were recommended by Shen (1982), Lyman et al. (1990), and Shen et al. (1993). For example, the empirical correlation which was recommended by Shen (1982) and Shen et al. (1993) can be written as

$$k_v = 22.05\,(1.024)^{T-20}\,U_s^{0.67}\,h^{-1.85} \quad , \qquad \text{hr}^{-1} \tag{4-71}$$

in which T is the temperature (°C), U_s is the water current (m/s), and h is the water depth (m). As an illustration, the liquid-side mass transfer coefficient, k_l, obtained from Eqs. 4-67 and 4-71 for B(a)P at 20°C is shown in Figure 4.4.

Example:

In order to estimate K_L for B(a)P for a neutral atmospheric condition, proceed along the following steps:

1) Select temperature, wind speed, and the correlation appropriate for the water body of interest.
2) Select a value of the Henry's Law constant from Table 4-5 and convert to dimensionless Henry's Law constant as per footnote (h) in Table 4-5.
3) Determine the value of k_l from a suitable correlation selected from Section 4.2.2 once a wind speed and type of water body are selected.

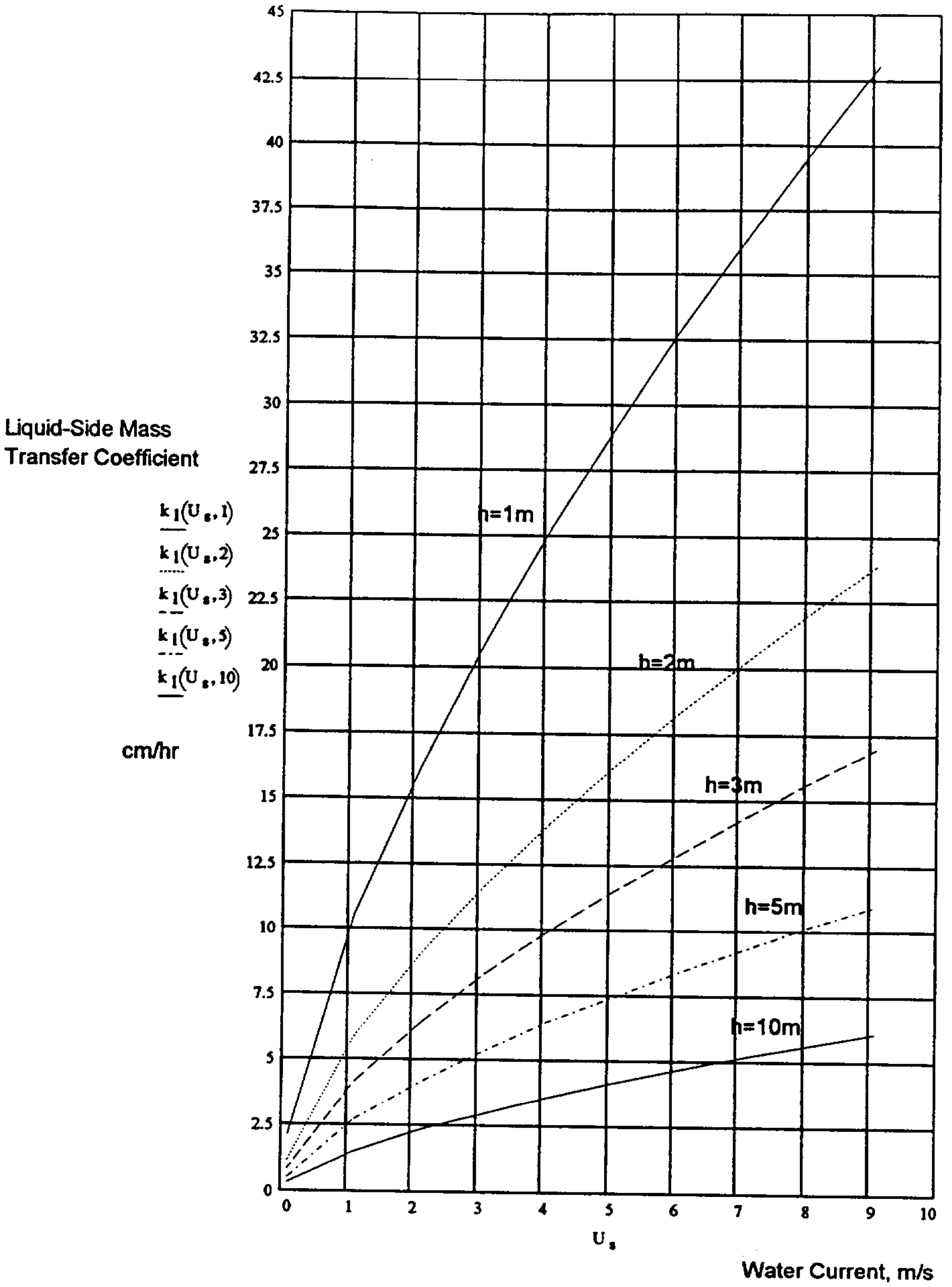

Figure 4.4. Liquid-Side Mass Transfer Coefficient for Benzo(a)Pyrene at 20°C for a Flowing River Based on Eqs 4-67 and 4-71 (h=river depth).

4) Determine k_g from either Eq. 4-49 or 4-50 depending on the resulting value for Re_o. Note that a value for U^*_a is required and this can be estimated from Eqs. 4-52, 4-58 - 4-60, and 4-61 or from wind speed profile data.
5) Use Eq. 4-48 to determine K_L.

As an illustration, consider the volatilization of B(a)P from a large water body (i.e., large reservoir or lake) at 20°C. The kinematic viscosities for the air and water phases were calculated to be 0.15 cm^2/s and 0.01 cm^2/s, respectively (Reid et al., 1987). The diffusion coefficients in air and water were estimated to be 0.049 cm^2/s and 4.9×10^{-6} cm^2/s, using Eq. 4-41 and 4-44, respectively. The gas-side mass transfer coefficient k_g at 20°C, obtained from Eqs. 4-49 and 4-50 (with linear interpolation of k_g in the region $0.13 \le Re_o \le 2$), and Eqs. 4-56 and 4-61 for z_o and C_D, respectively, is given, as a function of wind speed, in Figure 4.2. The liquid-side mass transfer coefficient, k_l, obtained from Eq. 4-63, at 20°C, is given in Figure 4.3. As an example, at U_{10} = 5 m/s, k_g = 1459 cm/hr (Figure 4.2) and k_l = 2.49 cm/hr (Figure 4.3). Thus, when a value of 0.0001 for the dimensionless Henry's Law constant is selected from Table 4-5, then

$$K_L = \left[\frac{1}{2.49} + \frac{1}{0.0001 \text{ x } 1459}\right]^{-1} = 0.14 \quad , \quad \text{cm/hr} \qquad (4\text{-}72)$$

Alternatively, one can directly determine K_L for B(a)P for the selected wind speed, using Figure 4.5. As can be seen from this example, the second term on the right hand side of Eq. 4-72 dominates with the liquid-side resistance ($1/k_l$) to B(a)P mass transfer across the water/air interface making up about 5.5% of the total resistance ($1\backslash K_L$) to mass transfer. Therefore, for B(a)P the gas phase resistance to mass transfer is the major B(a)P resistance to mass transfer. Also, as an approximation, for B(a)P $K_G \approx k_g$ for all wind speeds as can be verified by comparing Figures 4.5 and 4.6.

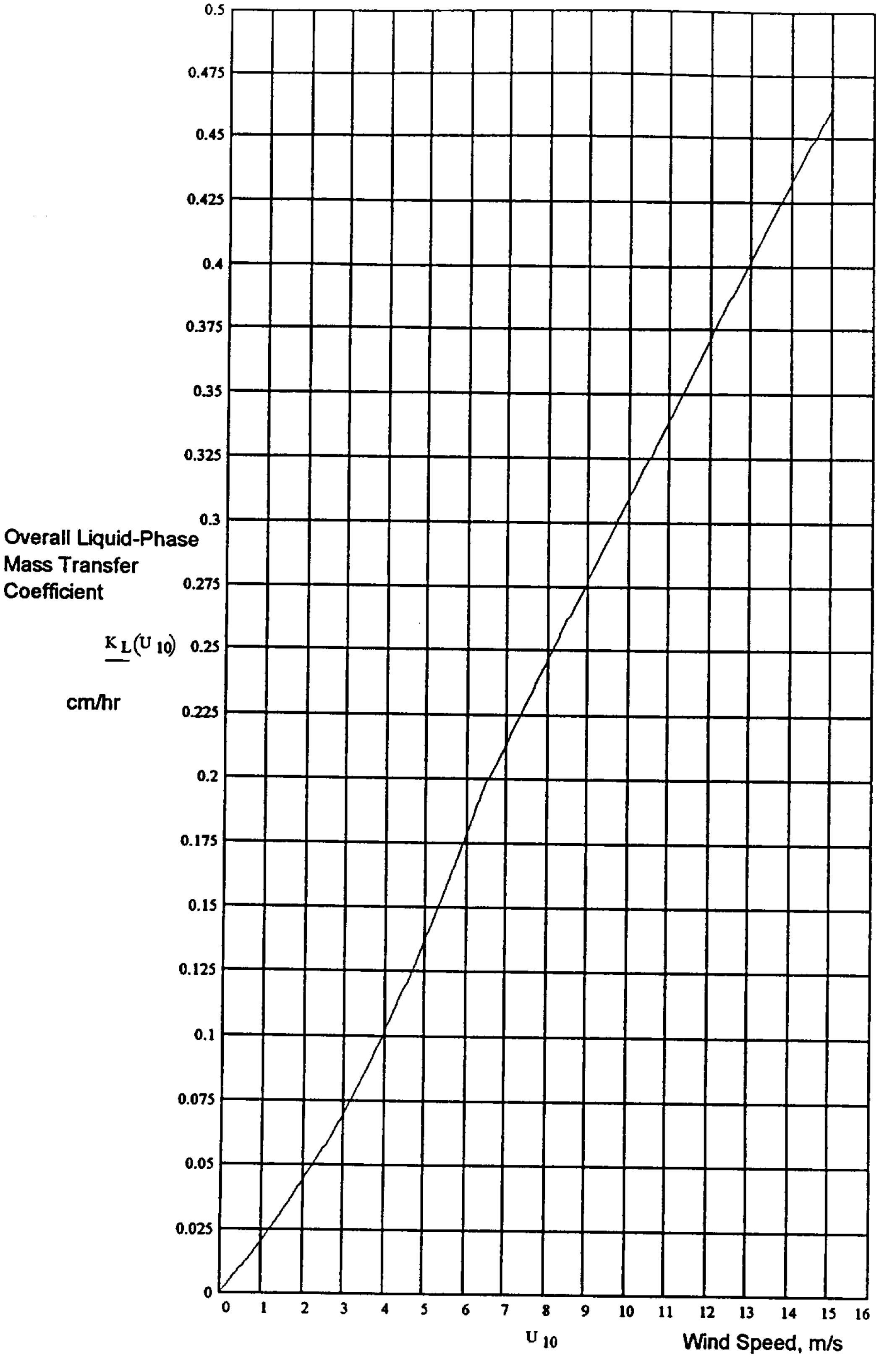

Figure 4.5 Overall Liquid-Side Mass Transfer Coefficient for Benzo(a)Pyrene for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlations of Cohen and Ryan, 1985 and Brutsaert, 1975).

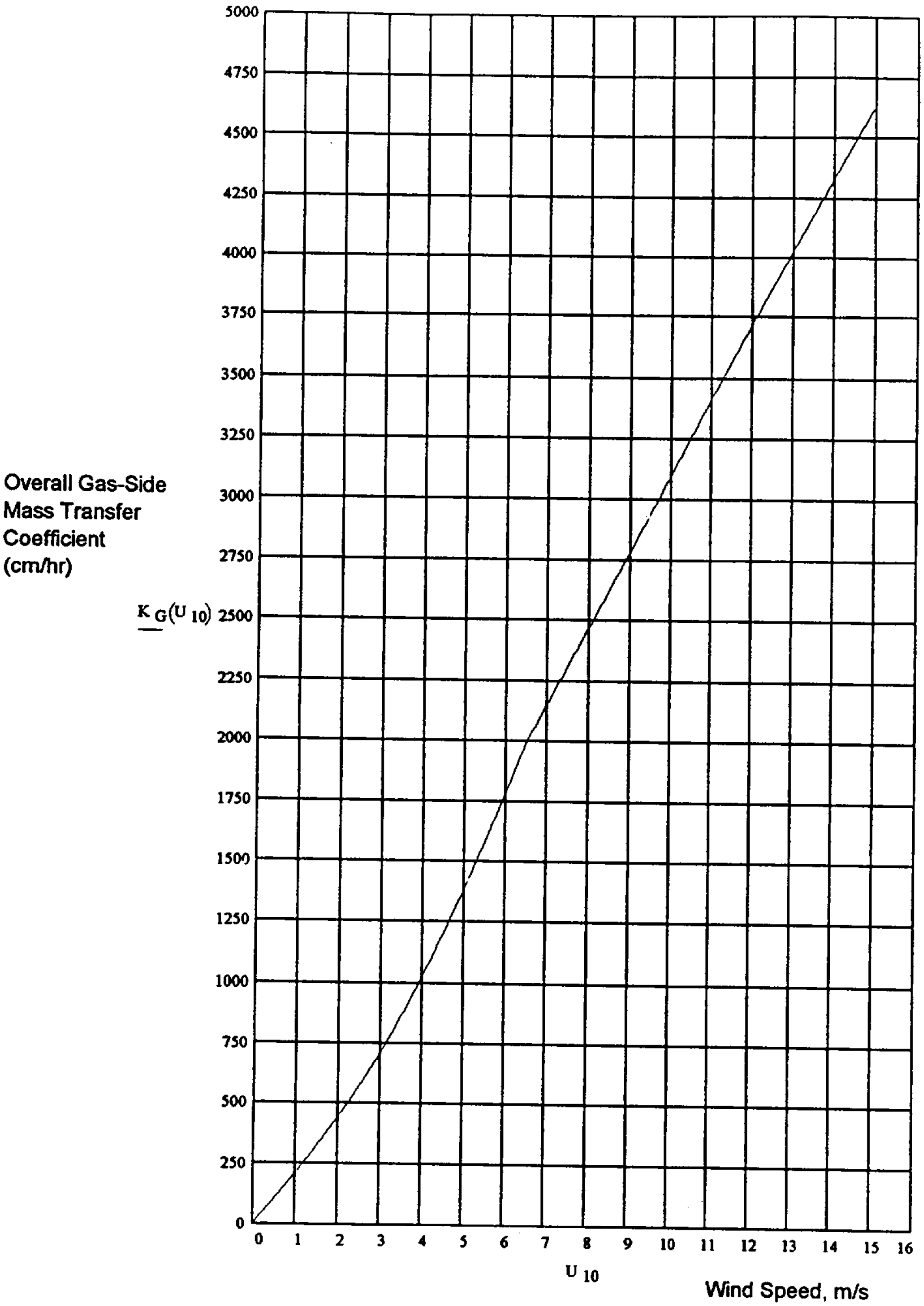

Figure 4.6 Overall Gas-Side Mass Transfer Coefficient for Benzo(a)Pyrene at 20°C for Water/Air Mass Transfer at Large Fetch. (Based on the Correlations of Brustsaert, 1975 and Cohen and Ryan, 1985).

4.3.3 Atmospheric Deposition

Atmospheric deposition is an intermedia transport process responsible for removing B(a)P from the atmosphere. Total atmospheric deposition is attributed to both dry and wet deposition. It is important to distinguish between deposition of B(a)P in vapor and particle-bound phases since different transport mechanisms are involved. Also, since different chemicals will reside in different portions of the particle size distribution, it is important to take into account both the particle-size distribution and the chemical distribution within the particle phase (Atkinson et al., 1990; Bidleman, 1988).

Since B(a)P has a low vapor pressure (see Table 4-2), it is expected to be present mostly in the particle-bound phase (Atkinson et al., 1990). Coutant et al. (1988) did not detect B(a)P in the vapor phase although Bidleman (1988) has estimated that approximately 95% of B(a)P should exist in the particulate phase in urban and background air. Thus, it is expected that the rate of dry and wet deposition of gaseous B(a)P is significantly less than that of particle-bound B(a)P.

4.3.3.1 Dry Deposition Velocity

Dry deposition may be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation (Davidson and Wu, 1989). Dry deposition is affected by a multiplicity of factors that often interact in complex ways. The most important factors are the atmospheric conditions, the nature of the surface, and physicochemical properties of the depositing species. Particles may be deposited and subsequently resuspended or they may adhere to the surface or may react chemically, producing irreversible changes in the deposited material. For gases, solubility and chemical reactivity at the deposition surface may also affect the dry deposition velocity. In general, dry deposition velocities can vary by several orders of magnitude depending on the surface characteristic (e.g., type of vegetative cover), the chemical type, and meteorological conditions.

B(a)P in Particle-Bound Phase

The flux of particle-bound pollutants from the atmosphere can be represented by the following equation:

$$N_a = V_d C_a^{(p)} \tag{4-73}$$

where $C_a^{(p)}$ is the mass of the pollutant in the particle phase per unit volume of air (e.g. $\mu g/m^3$), and V_d is the overall particle deposition velocity (m/s). The overall deposition velocity for the particle-bound chemical relates the rate of dry deposition to the ambient concentration (Bodek et al., 1988) and is defined as:

$$V_d = \int_0^\infty V_d(a) F(a) da \tag{4-74}$$

where $V_d(a)$ is the deposition velocity for particle diameter a, $F(a)$ is the normalized chemical distribution defined such that:

$$\int_0^\infty F(a) da = 1 \tag{4-75}$$

where $F(a)da$ is the mass fraction of the chemical present in particle phase in the size range a to $a+da$. The value of $F(a)$ can be determined either from an appropriate correlation (e.g. Junge correlation as defined in Section 4.2.6) assuming all particles absorb with equal tendency, or from appropriate experimental measurements. Given the distribution $F(a)$, the dry deposition of particle-bound B(a)P can be calculated given field data or appropriate models (Clay, 1992) for dry deposition of atmospheric particles as a function of particle size.

The dry deposition velocity can be estimated using a variety of prediction methods. In particular, for dry deposition of particles onto a vegetation canopy, the model of Slinn (1982) can be utilized to estimate the dry deposition velocity as a function of particle size.

Also, the simple correlations proposed by Whicker and Kirchner (1987), Baes et al. (1984) and Strenge and Napier (1989) can be used to estimate the dry deposition velocity as a function of the type and density (i.e., kg/m^2) of the vegetative cover. Dry deposition onto a water surface can be estimated using model of Williams (1982). The application of the above models in screening-level multimedia transport and fate models is discussed in the studies of Cohen (1986), Cohen et al. (1991), Clay (1992), and Chetty (1991). Table 4-12 presents values for deposition velocities of B(a)P in particle-bound phase as reported in a number of studies.

B(a)P in Vapor Phase

Dry deposition of gaseous B(a)P is expected to be of minor importance as an atmospheric loss process since only a small fraction of B(a)P is in the vapor phase (Atkinson, 1990). Experimentally determined values for dry deposition velocity of B(a)P in the vapor phase were not found in the literature. However, the method adopted by Cohen et al. (1990) can be used to estimate the dry deposition velocity. According to this approach, deposition velocity is proportional to $D^{2/3}$ (where D is the chemical molecular diffusivity in air). Thus, if the dry deposition velocity for a given reference chemical is known, the deposition velocity for B(a)P can be calculated using the equation

$$V_{d_B} = V_{d_A} \left(\frac{D_B}{D_A}\right)^{2/3} \qquad (4\text{-}76)$$

where V_{d_B} is the dry deposition velocity of B(a)P, V_{d_A} is the dry deposition velocity of a reference chemical for which the deposition velocity is known (was measured), at the desired meteorological and surface conditions, D_B is a diffusion coefficient of B(a)P, and D_A is a diffusion coefficient of the reference chemical.

Table 4-12. Dry Deposition Velocity(a) for B(a)P*

Deposition Velocity (cm/s)	Phase/Location	Reported Uncertainty	Temperature (K)	Wind Velocity (m/s)	Technique	Reference
0.23	N. Main St.†, Los Angeles	NR	Ambient Conditions 10/12/89; 10/16/89; 11/6-9/89	NR	Measured	Venkataraman, 1992(1)
0.09	Pico-Rivera‡, Los Angeles	NR	Ambient Conditions 2/16/89; 2/17/89; 2/21-23/89; 7/24-28/89	NR	Measured	Venkataraman, 1992(1)
0.16	Upland, Los Angeles	NR	Ambient Conditions 3/8-10/89; 3/13-14/89; 9/5/-6/89; 9/8/89; 9/11-12/89	NR	Measured	Venkataraman, 1992(1)
2.19	Air to Soil/ Southeast Ohio	NR	Ambient Conditions	5	Estimated	Ryan and Cohen (1986)(1)
0.361	Air to Water/ Southeast Ohio	NR	Ambient Conditions	5	Estimated	Ryan and Cohen (1986)(1)
0.22	Los Angeles	NR	NR	NR	Estimated◆	Clay, 1992(1)

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Dry deposition velocity is known to be a function of meteorological conditions, the nature of the surface, and properties of the depositing species (Davidson and Wu, 1989).

† Samplers were placed on the roof of a three-story building.

‡ Samplers were placed on a one-story building.

◆ Estimated by the Comprehensive Spatial-Multimedia Compartmental (COSMCM) model.

An illustrative calculation of deposition velocity for B(a)P: [The deposition velocity for SO_2 and CO_2 was given by Sehmel (1980; 1984)].

Calculation of V_d based on CO_2

CO_2: $V_{d_{CO_2}} = 0.3$ cm/s

$D_{CO_2} = 0.155\ \mathrm{cm^2/s}$ at 298K (Reid et al., 1987)

(1) - B(a)P

(2) - CO_2

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \tag{4-77}$$

$$V_{d_1} = 0.3\left(\frac{0.049}{0.155}\right)^{2/3} \tag{4-78}$$

$$V_{d_1} = 0.14\ \mathrm{cm/s} \tag{4-79}$$

Calculation of V_d based on SO_2

air: $M_A = 28.97$ g/mol (Lyman et al., 1990) SO_2: $M_{SO_2} = 64$ g/mol

$V_A = 20.1\ \mathrm{cm^3/mol}$ (Lyman et al., 1990) $V_{SO_2} = 41.1\ \mathrm{cm^3/mol}$ (Fuller et al., 1966)

Using Eq. 4-41, the diffusivity of SO_2 in air can be estimated as shown below

$$D_{SO_2} = \frac{10^{-3}\,(298)^{1.75}\,\sqrt{0.05}}{[(20.1)^{1/3} + (41.1)^{1/3}]^2} = 0.125\ \mathrm{cm^2/s} \tag{4-80}$$

$D_{B(a)P} = 0.049\ \mathrm{cm^2/s}$ at 298 K and 1 atm

$V_{d_{SO_2}} = 0.04\text{-}2.7$ cm/s for different deposition surfaces (0.04 cm/s was measured for asphalt and 2.7 cm/s was measured for an alfalfa surface)

(1) - B(a)P

(2) - SO_2

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \tag{4-81}$$

Lower Limit:

$$V_{d_1} = 0.04\left(\frac{0.049}{0.125}\right)^{2/3} = 0.021 \text{ cm/s} \tag{4-82}$$

Upper Limit:

$$V_{d_1} = 2.7\left(\frac{0.049}{0.125}\right)^{2/3} = 1.44 \text{ cm/s} \tag{4-83}$$

Thus, according to the above example, the deposition velocity for B(a)P is expected to be in the range of about 0.02 cm/s to 1.4 cm/s. It is noted, however, that since SO_2 is highly reactive in the aqueous phase, it is expected that a high estimate of the dry deposition velocity would be obtained when SO_2 is selected relative to CO_2 as the reference chemical. The actual value will depend on the prevailing meteorological conditions and surface characteristics in the area of interest. Therefore, the appropriate environmental and surface conditions should be selected for the reference chemical deposition velocity.

4.3.3.2 Wet Deposition

B(a)P in Particle-Bound Phase

Wet deposition (scavenging) can increase the overall deposition rate of particle-bound B(a)P and thus increase B(a)P concentration in the soil, water and vegetation due to direct deposition. Both rain and snow can remove B(a)P from air, however snowfall is not considered a significant removal process in most of the heavily populated regions in California. Rain scavenging of particles can be considered from two different perspectives.

One perspective is that rain scavenging provides a natural method of removing contaminants from the atmosphere. The other perspective is that rain containing the scavenged particles may also be considered a source of contamination for other environmental media (e.g., water, soil, vegetation).

The removal of particle-bound pollutants by rain scavenging can be determined from a chemical mass balance on the spectrum of raindrops as they travel to the ground. The chemical mass balance on a single rain drop is given by (Tsai et al., 1991)

$$\frac{d\left(C_w^{(p)}\,\frac{\pi D_d^3}{6}\right)}{d\tau} = \int_0^\infty E(a,D_d)\left(\frac{\pi D_d^2 L_c}{4L_c/V_t}\right) C_a^{(p)} F(a)\,da \qquad (4\text{-}84)$$

where

$C^{(p)w}$ = chemical concentration in rain water (e.g., ng/m^3 of water)

$C^{(p)}{}_a$ = chemical air phase concentration in the particle phase (ng/m^3 of air)

$E(a,D_d)$ = collection efficiency of a particle of diameter a by a raindrop of diameter D_d

$F(a)$ = the mass fraction distribution of the chemical in the particle phase, defined such that $F(a)da$ is the mass fraction of the chemical within the size fraction a to $a+da$

τ = travel time of a raindrop from the cloud base (e.g., s)

V_t = raindrop terminal velocity estimated from Easter and Hales (1984) (m/s)

L_c = height of the cloud base above ground level (e.g., m)

$$\begin{aligned} V_t(D_d) &= 40.55\,D_d, && D_d \leq 0.001\ \text{m} \\ &= 130(D_d)^{1/2}, && D_d > 0.001\ \text{m} \end{aligned} \qquad (4\text{-}85)$$

where D_d is the diameter of a raindrop (meters).

The collection efficiency can be approximated by the empirical correlation of Ryan and Cohen (1986), which is based on the field data of Radke et al. (1980). Recently, Tsai et al. (1991) demonstrated that the Ryan and Cohen (1986) correlation was of sufficient accuracy to describe field rain scavenging for PAHs. The collection efficiency is given by the following equation:

$$E(a) = \left[\frac{S - \frac{1}{12}}{S + \frac{7}{12}} \right]^{1.5} \quad , \quad a > 1.35\ \mu m \tag{4-86}$$

$$= 0.0005 \quad , \quad 0.09\ \mu m \le a \le 1.35\ \mu m$$

$$= 0.125/(0.5+a)^2 \quad , \quad a < 0.9\ \mu m$$

where $S = 0.1038a^2$ and a is the particle diameter (cm).

Given experimental data for *F(a)*, the average concentration of B(a)P in the particle-bound form can be obtained by integrating Eq. 4-84 over the spectra of raindrop sizes and particle sizes, between $\tau = 0$ (i.e., cloud base) and $\tau = L_c/V_t$ (i.e., the time to reach ground level). Accordingly, the following expression for B(a)P concentration in rainwater, at ground level, $\overline{Cw_f}$, is obtained

$$\overline{Cw_f} = \overline{Cw_o} + \frac{C_a}{V_r} \int_0^\infty \frac{3}{2} \frac{L_c}{D_d} \left[\int_0^\infty E(a)F(a)d(a) \right] \frac{\pi D_d^3}{6} N_{D_d} dD_d \tag{4-87}$$

in which C_a is the atmospheric mass concentration of the chemical in the particle-bound (e.g., ng/m^3), $\overline{Cw_o}$ is the average initial concentration at the cloud base, V_r is the volume of rain per volume of air given by

$$V_r = \int_0^\infty \frac{\pi D_d^3}{6} N_{D_d} dD_d \tag{4-88}$$

where N_D is the raindrop size distribution expressed such that $N_D dD_d$ is the number of raindrops per unit volume of air, between diameters D_d and $D_d + dD_d$. The raindrop size distribution, N_{D_d}, can be approximated by the Marshall-Palmer (1948) distribution.

$$N_{D_d} = N_o\, e^{-cD_d} \tag{4-89}$$

in which

$N_o = 0.08\ \mathrm{cm}^{-4}$

$C = 41 R_{Rain}{}^{-0.21}$

where the rate of rainfall, R_{Rain}, is expressed in units of cm/hr.

In the absence of field data for *F(a)*, the correlation of Junge (1977), along with the particle size distribution can be utilized using the rain scavenging model of Tsai et al. (1991).

An upper limit estimate of the "washout" ratio,

$$\Lambda_p^* = \frac{\overline{C_w^{(p)}}}{C_a^{(p)}} \tag{4-90}$$

can be obtained by considering the washout ratio at the beginning of the rain event. Following the analysis of Tsai et al. (1991), one obtains

$$\Lambda_p^* = \frac{\displaystyle\int_0^\infty \left\{ C_{wo}^{(p)} + \frac{3}{2} \frac{C_s^{(p)} L_c}{2D_d} \int_0^\infty E(a, D_d) \frac{\pi D_d^2}{4} n(a) da \right\} \frac{\pi D_d^3}{6} N_{D_d} dD_d}{C_a^{(p)} V_r} \tag{4-91a}$$

in which n(*a*) is the particle size distribution, $C_s^{(p)}$ is the concentration of the surface-bound chemical expressed on a surface-area basis (e.g., ng/m^2 of particle; i.e., $C_s^{(p)} = C_a^{(p)}/S_t$ where S_t is the surface area of particles per unit volume of air). Based on the work of Ryan and Cohen (1986), the rain scavenging ratio, Λ_p^*, for B(a)P can be estimated from

$$\Lambda_p^* \approx 720\ R^{-0.21} L_c \qquad (4\text{-}91b)$$

where R is the rate of rainfall (mm/hr) and L_c is the height of the cloud base (m).

B(a)P in Vapor Phase

Wet deposition is often expressed using a washout ratio, W, defined as

$$W = C_{rainwater}/C_{air} \qquad (4\text{-}92)$$

in which the chemical concentration in the rain is related to that in the ambient air (Atkinson et al., 1990). Since the solubility of B(a)P in water is low, it appears that wet deposition of gaseous B(a)P will be of relatively minor importance as a loss process for this compound. Although no data exist concerning the wet deposition for gaseous B(a)P, rain scavenging of the vapor component of B(a)P can be predicted using the approach described by Tsai et al. (1991) and Clay (1992).

An upper-limit estimate can be obtained by assuming that the raindrops are in equilibrium with the air phase when they reach ground level. Accordingly, the concentration of the dissolved chemical in rain, $C_w^{(d)}$ (ng/m^3 water), is given by

$$C_w^{(d)} \approx \frac{C_a^{(g)}}{H_{aw}} \qquad (4\text{-}93)$$

in which $C_a^{(g)}$ is the concentration of the chemical in the atmosphere in the vapor phase (e.g., ng/m^3 air), and H_{aw} is the dimensionless Henry's Law constant (i.e., $H_{aw} = C_a^{(g)}/C_w^{(d)}$). Thus, by comparing Eqs. 4-92 and 4-93, it follows that the maximum value of the washout ratio for B(a)P vapor is given as

$$W = 1/H_{aw} \qquad (4\text{-}94)$$

4.3.4 Resuspension

Particle induction to the atmosphere from the soil environment due to wind and mechanical erosion could present a significant exposure via the inhalation pathway. For particles <50 microns, the resuspension process can be induced by both mechanical and wind disturbances which provide sufficient energy to overcome gravitational forces and allow particles to be dispersed by the wind. Since a fraction of the resuspended particles may be small enough (i.e., $<10\mu$m) to reach the lower respiratory tract, it may be necessary to consider the impact of wind resuspension of contaminated soil on exposure to B(a)P.

Cowherd et al. (1988) provided an assessment methodology that can be used to estimate the wind erosion of soil particles. The procedure is based on characterizing the surfaces from which particles may be resuspended into two categories: (1) "limited reservoirs" characterized by a non-homogeneous surface (e.g., a mixture of gravel, sticks, sporadic vegetative life) and where wind erosion is retarded by various features of the terrain; and (2) "unlimited reservoirs" characterized by a uniform surface (e.g., agricultural soil) with a low threshold friction velocity. The above approaches can be conveniently incorporated into multimedia transport and fate models as shown by Clay (1992).

4.4 Degradation of B(a)P

4.4.1 Reaction Half-life in Air

The following subsections discuss the specific degradation processes that were considered most applicable to B(a)P and the corresponding findings of the literature survey.

However, one is cautioned that since some of the reaction rate parameters have been obtained at elevated pollutant concentrations (i.e., ppm range) the resulting rate constants may, or may not, apply to actual ambient conditions. Reported values of photolysis and reaction half-lives and rate constants for reaction of adsorbed B(a)P in air are summarized in Table 4-13.

4.4.1.1 Photolysis of Adsorbed B(a)P

After emission from combustion sources, adsorbed B(a)P travels through the atmosphere where it can undergo photodegradation. This reaction pathway may be influenced by several factors such as ambient humidity, temperature, solar intensity, and physical and chemical characteristics of the absorbent.

Ambient humidity seems to be a factor in the rate of degradation of adsorbed B(a)P by photolysis. Kamens et al. (1988) observed that daytime B(a)P decay was slower under low ambient humidities than high humidities. The authors also observed that the decay rate of B(a)P was slower when B(a)P particle loading was in the range of 30-350 ng/mg than in the range of 1000-2000 ng/mg. The reaction half-lives are reported in Table 4-13.

Sunlight intensity affects the degradation of B(a)P. Kamens et al. (1988) showed that the B(a)P decay constant (assuming a first-order reaction) is directly proportional to solar intensity. Valerio et al. (1991) also studied the effects of solar intensity on B(a)P absorbed onto airborne particulate matter and found the concentration of B(a)P to be inversely proportional to solar intensity consistent with the earlier observation of Kamens et al. (1988).

The photolysis rate of adsorbed B(a)P appears to be strongly dependent on the substrate to which it is adsorbed. Yokley et al. (1986) observed significant phototransformation of B(a)P occurred when it was adsorbed onto particles of silica gel, alumina, and controlled-pore glass. However, B(a)P did not undergo significant phototransformation when adsorbed to various stack ashes from bituminous and subbituminous

Table 4-13. Photolysis and Reaction Half-Lives and Rate Constants for Reaction of Benzo(a)pyrene Adsorbed to POM in Air*

Reaction/ Photolysis Half-Life(a) (hrs)	Reaction/ Photolysis Rate Constant in Air	Reported Value	Reported Units	Conditions	Temperature	Technique	References	Source Cited
168	0.101±0.023 day^{-1}	7	days	Reaction with 10 ppm NO_x	NR	Experimental	Butler and Crossley, 1981(1)	
1.284	0.0090(a) min^{-1}	0.0090	min^{-1}	30-350 ng/mg PAH particle loading(b)	14.6°C	Experimental	Kamens et al., (1988)(1)	
0.548	0.0211(a) min^{-1}	0.0211	min^{-1}	1000-2000 ng/mg PAH particle loading(b)	14.6°C	Experimental	Kamens et al., (1988)(1)	
0.5	0.0234 min^{-1}	0.5	hr	Light Intensity = 1 $\text{cal/cm}^2\text{min}$ 10 g/m^3 H_2O(b)	20°C	Experimental	Kamens et al., (1988)(1)	
2.1	0.0234 min^{-1}	2.1	hr	Light Intensity = 0.8 $\text{cal/cm}^2\text{min}$ 4 g/m^3 H_2O(b)	0°C	Experimental	Kamens et al., (1988)(1)	
6	0.0234 min^{-1}	6	hr	Light Intensity = 0.4 $\text{cal/cm}^2\text{min}$ 2 g/m^3 H_2O(b)	-10°C	Experimental	Kamens et al., (1988)(1)	
144	4.81×10^{-3} hr^{-1}	6	days	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	U.S. EPA, 1986(1)

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) First order rate constant.

(b) Photolysis experiments.

coal, or flaked graphite. The data seem to indicate that any ashes with greater than 10% iron and/or 0.5% carbon repressed the phototransformation of B(a)P. This conclusion appears to be supported by an earlier study of Griest and Tomkins (1984) who showed that the higher the carbon content of the ash particle, the higher the concentration of the adsorbed PAH. In addition, the unique composition, color, and porosity of various ashes may contribute to the different photoreactivities of adsorbed B(a)P. Significant inner filter suppression of photolysis of adsorbed B(a)P was observed on substrates that are highly colored and relatively porous (Nielsen et al., 1983; Wehry, 1971). To investigate the effect of adsorbent color on the photoreactivity of adsorbed B(a)P, Yokley et al. (1986) categorized the adsorbents using the Munsell soil color charts and concluded that light colored adsorbents exhibited efficient photodegradation but dark colored substrates seemed to inhibit the photodegradation of adsorbed B(a)P.

Peters and Seifert (1980) studied the behavior of B(a)P adsorbed to a natural dust matrix under atmospheric conditions. ^{14}C-B(a)P was deposited on dust-coated and dust-free glass fiber filters. These filters were exposed for 24 hours to 400-W halogen radiation which corresponds to the conditions of a bright sunny day. The ambient air contained approximately 30 ppb of ozone. This experiment was also conducted under the same conditions in the dark. Data from dust-coated and dust-free filters in both dark and light conditions were compared and they indicate that sunlight accelerates the degradation of adsorbed B(a)P significantly. However, the presence of dust (particulate matters) did not seem to affect the reactivity of adsorbed B(a)P.

4.4.1.2 Reaction of Adsorbed B(a)P with Ozone (O_3)

Pitts et al. (1986) investigated the effects of adsorbent, ozone concentration, and humidity on the reactivity of adsorbed PAH, including B(a)P. The adsorbents studied included glass fiber (GF) and Teflon impregnated glass fiber (TIGF) filters as well as ambient POM. The concentrations of ozone ranged from 50 to 290 ppb and the relative humidity (RH) ranged from 1 to 50%. In a passive exposure system, the amount of adsorbed B(a)P reacted (~50 to 60%) did not vary significantly with increasing ozone concentrations or RH for both filters. In an active flow system, it was shown that the reaction of B(a)P adsorbed on GF and TIGF filters exposed to 200 ppb ozone was rapid at 1% RH.

In other experiments, ambient POM was collected near a freeway in Riverside in the morning hours (0600-1000) so that the freshly emitted particulates were not exposed to significant levels of ozone. The POM was adsorbed on GF and TIGF filters and exposed passively to 200 ppb ozone at 1 and 50% RH for 3 hours. The percentage of adsorbed B(a)P that reacted at 1% RH was approximately 70 and 80% for both filters, while at 50% RH approximately 40 and 70% reacted for GF and TIGF filters, respectively. The decrease in reactivity of B(a)P adsorbed on the GF filter may be due to the competition of B(a)P with water for adsorption sites. Pitts et al. (1986) concluded that at an ambient ozone level of 200 ppb and RH between 1 and 50% in the Los Angeles air basin, significant degradation of PAH (including B(a)P) can occur.

Pitts et al. (1978) verified that adsorbed B(a)P reacted with elevated concentrations of pollutant gases under simulated atmospheric conditions. Experiments were conducted with B(a)P deposited on washed and fired glass fiber filters and exposed in the dark to particle-free, pure air containing either O_3 at 11 ppm for 24 hours, NO_2 at 1.3 ppm for 24 hours, or PAN at 1.1 ppm for 16 hours. Reaction products showed that B(a)P reacted with O_3 and PAN to form a variety of oxygenated products and with NO_2 to form nitro-derivatives. The exposure of adsorbed B(a)P to 1 ppm of NO_2 which contained trace amounts of HNO_3 (~10 ppb) resulted in the detection of three nitrated compounds: 6-nitro-B(a)P, 1-nitro-B(a)P, and 3-nitro-B(a)P isomers. The authors also conducted an experiment which exposed B(a)P deposited on glass fiber filters to ambient Riverside smog for 72 hours during the day (6am-9pm) and night (9pm-6am). No nitro-B(a)P was detected in this experiment. This may be due to either the low concentration of NO_2 in Riverside smog, or the removal of HNO_3 from the upstream filter. Furthermore, it was possible that prolonged exposure to oxidizing species degraded the nitro-derivatives that might have been formed. The authors emphasized the fact that since the experiments were conducted with PAH adsorbed on the surface of glass fiber filters, it was inconclusive whether PAH adsorbed on the surface of airborne particles would react in the same manner because atmospheric reactions of PAH may be affected by multiple factors such as surface chemistry, ambient pollutant concentration, particle size, sunlight intensity, atmospheric mixing, and transport time.

In additional studies, Pitts et al. (1980) examined the behavior of adsorbed B(a)P when exposed to ozone. B(a)P was deposited on glass fiber filters in an apparatus that allowed the B(a)P to be exposed to O_3 either in the dark or under actinic ultraviolet illumination. Experiments were typically 4 hours in duration with the concentration of ozone ranging from 190 to 210 ppb. The data indicate that approximately 50% of the B(a)P was degraded in the first hour of exposure in the dark. After the four-hour period, approximately 80% was degraded. Analysis of the results showed that B(a)P-4,5-oxide was the major stable reaction product. The authors suggested that this stable oxide may be capable of forming and surviving for significant time periods in the atmospheric cycle including particulate emission, atmospheric transport and transformation, and ultimate deposition. It is not clear from these data whether ozonolysis could occur between inhaled photochemical smog and adsorbed B(a)P on particles already deposited in the lung.

Peters and Seifert (1980) observed that the concentration of adsorbed B(a)P was inversely proportional to the daily average ozone concentration. Since this effect was observed at an ozone concentration of less than 50 ppb and an ambient temperature of 20°C, the authors predicted that ozonation of adsorbed B(a)P would be more pronounced during summer days with high ozone concentrations and ambient temperatures.

Van Vaeck and Van Cauwenberghe (1984) studied the interaction of O_3 with 10 PAH (including B(a)P) in diesel exhaust particulate matter adsorbed on glass fiber filters. The filters were exposed to 1.5 ppm of O_3 in particle free air for periods ranging between 0.5 and 4.0 hours. The yields of conversion products from adsorbed B(a)P and ozone after 0.5 to 4 hours ranged from 62 ± 7 to $87 \pm 3\%$, respectively. The authors concluded that adsorbed B(a)P with O_3 could yield significant conversion in a few hours at O_3 levels typical of photochemical smog episodes.

Coutant et al. (1988) studied the reaction of adsorbed B(a)P with ozone in the summer and the winter in Columbus, Ohio. The decline in adsorbed B(a)P concentration did not exceed 10% after exposure to O_3. No evidence of volatilization was found. The authors strongly suggested that oxidative losses of B(a)P adsorbed on ambient airborne particulate matter due to ozonolysis were negligible at ambient levels of ozone.

4.4.1.3 Reaction of Adsorbed B(a)P with OH Radicals

No studies had been conducted on the reaction of adsorbed B(a)P with OH radicals.

4.4.1.4 Reaction of Adsorbed B(a)P with Oxides of Nitrogen

Reaction with NO_2 and HNO_3

Yokley et al. (1985) showed that in the presence of nitric acid-free NO_2 at 95 ppm, adsorbed B(a)P failed to undergo detectable non-photochemical transformation. However, NO_2 at 95 ppm that was not scrubbed of nitric acid facilitated the non-photochemical degradation of B(a)P adsorbed on silica gel. Depending on the substrate (e.g., Texas lignite ash, commercially-available analytical standard ash, silica, and alumina), adsorbed B(a)P underwent detectable photochemical degradation regardless of the presence of NO_2 or HNO_3. The authors used a very high concentration of NO_2 and HNO_3 (95 ppm and 12 ppm, respectively) to study the effect of these compounds on the photo/non-photodegradation of adsorbed B(a)P. However, these high levels of NO_2 and HNO_3 are far from typical of the ambient environment; therefore, the results of these experiments may not be relevant to the potential for reaction of NO_2 or HNO_3 with adsorbed B(a)P.

Reaction with N_2O_5

Pitts et al. (1985) studied the reactivity of adsorbed B(a)P on glass fiber filters with N_2O_5 in the dark. The samples were placed into a ~360-L all-Teflon chamber filled with purified matrix air of ≤5% relative humidity at ~295 K and were exposed to a stream of N_2O_5

(~9 ppm) with trace amounts of NO_2 (1 or 10 ppm), HNO_3 (~1 ppm), and NO_3 (0.01 or 0.001 ppm, as a result of thermal degradation of N_2O_5). The maximum NO_2-B(a)P yields after 30 minutes for the various exposure systems were 9 and 11%. The most abundant mononitro-derivative formed was 6-NO_2-B(a)P. Traces of 1- and 3-NO_2 isomers were also detected. Adsorbed B(a)P was also exposed to NO_2 at 10 ppm and HNO_3 at ~0.1 or 1.5 ppm. After 30 minutes, the maximum NO_2-B(a)P yields were 4 and 5%. When adsorbed B(a)P was exposed to HNO_3 alone at 1.5 ppm, no nitro-derivatives were detected.

Reaction with NO_x

Butler and Crossley (1981) conducted a study on the behavior of B(a)P adsorbed to soot particles when exposed to 10 ppm of NO_x over a period of 51 days. Decreasing concentrations of B(a)P were observed after 5, 12, 21, 29, and 51 days of exposure. The concentration of B(a)P changed from an initial concentration of 1557 mg/kg to a final concentration of 31 mg/kg. Results of the experiment indicate that B(a)P had a half-life of 7 days with a corresponding rate constant of 0.101 ± 0.023 day^{-1}. The authors claimed that the experimental condition represents the behavior of adsorbed B(a)P on soot particles in a heavily polluted ambient aerosol and concluded that nitration of atmospheric PAH can be an effective and important removal mechanism because it is capable of converting carcinogenic B(a)P to noncarcinogenic 6-nitro-B(a)P.

Reaction with NO_2

Ramdahl and Bjorseth (1984) studied the effects of ambient concentration of NO_2 and various adsorbents on the reactivity of adsorbed PAH, including B(a)P, in a fluidized bed reactor which simulates the behavior of particles in the atmosphere. B(a)P was adsorbed on silica, alumina, and activated charcoal and was exposed to 0.5 ppm of NO_2 containing a trace amount of nitric acid for 16 hours in the dark. Reaction products demonstrate the reactivity of adsorbed B(a)P on various adsorbents to be in the following order: silica > alumina > activated charcoal; the corresponding percentage yields of 6-nitro-B(a)P for the adsorbents were 5%, 0.6%, and non detectable, respectively. Since the experimental NO_2 concentration was similar to the ambient NO_2 concentration, the authors concluded that nitration of PAH in the atmosphere was likely to occur.

Brorström et al. (1983) studied the reaction of adsorbed B(a)P with NO_2 and O_3 during high-volume sampling of airborne particulate matter. The samples were exposed to approximately 950±50 ppb of NO_2 and 200 ppb of O_3 for 24 hours. Results indicate that adsorbed B(a)P degraded when exposed to various concentrations of NO_2: 30, 100, and 200 ppb at temperatures ranging from -5 to O°C. The corresponding average percentage degradation for the three exposure systems was 3, 10, and 19%, respectively. The authors concluded that about 20% degradation of adsorbed B(a)P can occur under very unfavorable conditions within the range of NO_2 concentrations in urban air.

4.4.1.5 Reaction of Adsorbed B(a)P with SO_2

Butler and Crossley (1981) studied the behavior of B(a)P adsorbed on soot particles when exposed to ambient laboratory air for 231 days as well as air containing 5 ppm SO_2 for 99 days. Reaction products were analyzed and the two sets of results were compared. The mean B(a)P concentrations were not significantly different (1272±117 and 1246±249 for ambient laboratory air and air containing 5 ppm SO_2, respectively). The authors concluded that the B(a)P/soot system appeared relatively stable towards ambient laboratory air and air containing 5 ppm SO_2.

4.4.1.6 Reaction of Adsorbed B(a)P with Selected Pollutants

Grosjean et al. (1983) investigated the reaction of adsorbed PAH with atmospheric pollutants. A mixture of 0.19±0.01 μg of B(a)P, 0.97±0.05 μg of perylene, and 15.5±0.08 μg of 1-nitropyrene was adsorbed on glass fiber and teflon filters coated with fly ash, diesel exhaust, and ambient particles and was exposed to either pure air, ~100 ppb of ozone, ~100 ppb of SO_2, ~100 ppb of nitric acid-free NO_2, or particle-free ambient air in the dark for 3 hours. Results indicate that there was no chemical or physical removal of the three PAH regardless of filter type, carrier particles, or atmospheric pollutants.

4.4.2 Reaction Half-life of B(a)P in Water

Factors such as pH, salinity, temperature, and singlet oxygen concentration influence the degradation of B(a)P in the aquatic environment. Reaction half-lives of B(a)P in water are summarized in Table 4-14.

Lee (1977) indicated that degradation rates of B(a)P in the water was found to be very low in the Skidaway estuarine where the source of B(a)P was from boating traffic. It was also shown that the degradation rate of hydrocarbons was significantly lower in the winter than in the summer. In another experiment, Lee et al. (1978) studied the degradation of B(a)P in a controlled ecosystem enclosure. It was found that in the top 5 m in surface waters, photooxidation was an important removal process for B(a)P. The authors also reported the half-life of B(a)P in water from depuration studies with oysters to be 18 days.

Zepp and Schlotzhauer (1979) reported the following equation for predicting photolysis rates of PAH in natural water bodies at depth z:

$$-\left(\frac{d[A]}{dt}\right)_{z,\lambda} = \sum \phi_{r,\lambda}\, k_{z,\lambda}\, [A] = k_{p,z}\, [A] \tag{4-95}$$

where $\phi_{r,\lambda}$ is the quantum yield at wavelength λ, $k_{z,\lambda}$ is the specific sunlight absorption rate of aromatic hydrocarbons at wavelength λ and depth z, and $\left(\frac{d[A]}{dt}\right)$ is the photolysis rate of the aromatic hydrocarbon in a water body at depth z. The total photolysis rate can be obtained by integrating over the effective range of wavelengths. The half-life can then be calculated using the equation:

$$t_{1/2} = \frac{0.693}{k_{p,z}} \tag{4-96}$$

The half-life of B(a)P for direct photochemical transformation was calculated to be 0.54 hr.

Table 4-14. Reaction Half-Lives of Benzo(a)pyrene in Water*

Reaction Half-Lives (hrs)	Reported Value	Reported Units	Condition	Temperature	Technique	References	Source Cited
432	18	days	From depuration studies with oysters	NR	Measured	Lee et al., 1978(1)	
1.1	1.1	hr	20% acetonitrile in pure water	Midmorning sunlight, late January	Measured	U.S. EPA, 1978(1)	
0.7	0.7	hr	20% acetonitrile in pure water	Noon sunlight mid-December	Measured	U.S. EPA, 1978(1)	
0.54	0.54	hr	Direct photochemical transformation	Midday, midsummer Latitude 40° N	Calculated	Zepp and Schlotzhauer, 1979(1)	U.S. EPA, 1978(1)
1.5×10^3	1.5×10^3	hr	Photosensitized oxygenation	Midday, midsummer Latitude 40° N	Calculated	Zepp and Schlotzhauer, 1979(1)	
76.8	3.2	days	No partitioning	Summer day Latitude 40° N	Calculated	Zepp and Schlotzhauer, 1979(1)	
312	13	days	With partitioning	Summer day Latitude 40° N	Calculated	Zepp and Schlotzhauer, 1979(1)	
9.6	0.40	days	NR	NR	NR	U.S. EPA, 1986(1)	
20148	20148	hr	NR	NR	NR	Hattemer-Frey and Travis, 1991(1)	Herbes et al., 1979

NR=Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

Zepp and Schlotzhauer (1979) also studied the effect of photosensitized oxygenation of singlet oxygen on the photolysis rate of B(a)P. The equation for calculating the reaction half-life at near-surface steady-state concentrations of singlet oxygen $[^1O_2^*]$ is as follows:

$$t_{1/2} = \frac{0.693}{k_A[^1O_2^*]} \tag{4-97}$$

where $[^1O_2^*]$ was assumed to be 6×10^{-12}M in summer. The photosensitized oxygenation half-life of B(a)P is calculated to be 1.5×10^3 hr. The half-lives of B(a)P obtained from equations 4-90 and 4-91 show that the direct photolysis process was more rapid than the photosensitized oxygenation process. The authors concluded that singlet oxygen does not appear to play a significant role in the photochemical transformation of the PAH in the aquatic environment (i.e., the upper 35 meters mixed layer of the ocean). For turbid rivers, photolysis of PAH is significantly retarded due to light attenuation and partitioning of PAH to bottom sediment where it is dark. Calculated half-lives of B(a)P in a 5-meter deep inland water body with and without partitioning are 13 and 3.2 days, respectively.

4.4.3 Biodegradation Half-Life in Sediment and Water

Several factors affect the rate of biodegradation of B(a)P in water and sediments. In general, PAH biodegradation rates are inversely proportional to the number of fused benzene rings and are further hindered by ring substitution (Cerniglia and Heitkamp, 1989). The authors also reported that PAH biodegradation rates increase with temperature. Using estuarine sediments, Deluane et al. (1981) demonstrated that degradation rates of B(a)P increased significantly with increasing pH and increasing redox potential.

Gardner et al. (1979) studied the degradation of B(a)P in an aquatic sediment environment contaminated with crude oil using three different types of sediment: marsh sediment, medium sand, and fine sand with and without the benthic polychaete worm, Capitella capitata. Of the four PAH examined, B(a)P had the slowest degradation by microbes. The degradation rate of B(a)P in the surface sediments was found to be less than 2 ng of B(a)P/g of wet sediment/72 hours. Microbial degradation was more rapid in the top layers of the sediments than in the lower layers. However, with the presence of *C. capitata*, degradation of B(a)P was 2 to 2.35 times faster than in the absence of *C. capitata*.

Lee (1977) found that B(a)P adsorbs to sediments beneath detritus and falls to the bottom of the ecosystem. Therefore, degradation was a result of interaction of microfauna, meiofauna, and macrofauna instead of free-floating bacteria. In another study, Lee et al. (1978) showed that loss of B(a)P due to microbial degradation was not important because B(a)P was found to be associated with detrital particles consisting of dead phytoplankton cells and bacteria instead of with living phytoplankton cells. Lu et al. (1977) also studied soil microbial degradation of B(a)P under laboratory conditions. They reported that B(a)P was resistant to degradation and the half-life was approximately 152 weeks. However, Poglazova et al. (1971) reported that degradation of B(a)P was rapid by various soil microflora.

Shiaris (1989) concluded that the magnitude of the biodegradation rate was proportional to the ambient PAH concentrations in estuarine sediments. In addition, the turnover time (the time required for the entire pool of PAH in a given sample to be transformed) increases with increasing molecular weight. Of the three sites studied, the transformation rates at two sites were affected by temperature and salinity, but not by pH. B(a)P was more resistant to transformation than other PAH studied and it has the longest turnover times: 53.7 to 83.3 days as opposed to 8 to 20 days for other PAH. The transformation products consist of CO_2, polar metabolites, and residual fraction. The major transformation product of B(a)P was the polar metabolite fraction. This suggests that the high-molecular weight PAH are only partially degraded in sediments. As a result, the turnover times may be underestimated. Finally, Shiaris (1989) conducted a series of experiments on the degradation of B(a)P, in sediments by following the rate of transformation of radioactive-labelled B(a)P.

A summary of biodegradation half-lives and rate constants obtained from the literature is presented in Table 4-15.

Table 4-15. Biodegradation Half-Lives, Rates, and Turnover Times(a) for Benzo(a)pyrene in Soil, Sediment and Water*

Biodegradation Half-Lives (days)	Biodegradation Rate Constant	Turnover Time	Medium	Temperature (°C)	Technique	References	Source Cited
1048	4.63×10^{-3}wk^{-1} (b)	NR	Drummer Soil	26.7	Experimental	Lu et al., 1977(1)	
NR	2 ng/g sediment per 72 hr	NR	Sediment	20	Experimental	Gardner et al., 1979(1)	
>1400	NR	>2800 days to >4200 days	Freshwater and estuarine sediment ecosystem	22	Experimental	Cerniglia and Heitkamp, 1989(1)	Heitkamp and Cerniglia, 1987(1)
NR NR NR	0.15 ng/h per g 1.72 ng/h per g 49.5 ng/h per g	53.7 days 82.3 days 80 days	Estuarine sediment	2-22	Experimental	Shiaris, 1989(1)	
NR	NR	1246 days	Petroleum contaminated sediment and water	12	Experimental	Cerniglia and Heitkamp, 1989(1)	Herbes and Schwall, 1978(1)
NR	NR	2000 to 9000 days	Estuarine water	10	Experimental	Cerniglia and Heitkamp, 1989(1); Shiaris, 1989(1)	Readman et al., 1982(1)
480	NR	NR	Soil	NR	NR	U.S. EPA, 1986(1)	
5475	5.3×10^{-6}hr^{-1} (c)	NR	Soil	NR	NR	Hattemer-Frey and Travis, 1991(1)	Lu et al., 1977(1)
839.5	3.4×10^{-5}hr^{-1}	NR	Water	NR	NR	Hattemer-Frey and Travis, 1991(1)	Herbes et al., 1979

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Turnover time = the time required for the entire pool of PAH in a given sample to be transformed.

(b) Calculated based on the data of Lu et al. (1977).

(c) The half-life reported by Hattemer-Frey and Travis (1991) contradicts the half-life calculated from the data reported by Lu et al. (1977).

5.0 CONCLUSIONS AND RECOMMENDATIONS

NOMENCLATURE

- The utilization of both the American and the European numbering systems for polycyclic aromatic hydrocarbons has led to a considerable degree of confusion in the literature. The synonyms for B(a)P can sometimes be mistaken for B(e)P and vice versa; therefore, one should be careful when conducting a literature research.

DEGRADATION PROCESSES

- The most effective degradation processes for B(a)P are photochemical degradation, reaction with atmospheric pollutants such as O_3 and NO_x.

- Depending on the soil microflora, biodegradation can be a significant degradation mechanism for B(a)P.

- The reactivity of adsorbed B(a)P is dependent on how it is bound by atmospheric particles. If B(a)P is adsorbed on the surface of the particle, it is available for degradation reactions; if B(a)P is integrated into the particle, then chemical degradation may be insignificant.

TRANSPORT PROCESSES

- B(a)P is transported throughout the environment primarily in the particle-bound form.

- Dry deposition and rain scavenging of particle-bound B(a)P dominate the intermedia transfer of B(a)P from air to the terrestrial and aquatic environments.

The evaluation of intermedia transfer factors for B(a)P suggests that the following issues may require further consideration:

- When reviewing literature on B(a)P, one should ensure that B(a)P and not B(e)P is the compound being discussed. Original references should be obtained to check for the compound structure, if available.

- Biodegradation of B(a)P has traditionally been considered negligible. However, certain microflora have been reported to degrade B(a)P rapidly. Therefore, experimental studies in this area as needed.

- Studies regarding bioconcentration factors for B(a)P are scarce. Future studies should be conducted on the bioconcentration factors in different media, milk, beef, and vegetation.

- Reported Henry's Law constants for B(a)P differ by about 80%. Since this is the main parameter used to predict air/water partitioning it is critical that experimental measurements be revisited.

- Although some dry deposition velocity data exist for B(a)P, this area should be investigated further because dry deposition is a major intermedia transfer mechanism for B(a)P. Also, estimates of the dry deposition of B(a)P can be refined by considering the chemical mass distribution of B(a)P as a function of particle size.

- Rain scavenging of B(a)P can result in significant wet deposition of B(a)P onto the terrestrial and aquatic environments. Estimated of the wet deposition, as in the case of dry deposition, can be refined by considering the chemical distribution of B(a)P as a function of particle size.

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Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume II: Metals and Non-Volatile Organic Compounds
Section 4 - Mercury

Prepared by:

Yoram Cohen
Department of Chemical Engineering
National Center for Intermedia Transport Research

Arthur M. Winer
Environmental Science and Engineering Program
School of Public Health

Research Associate:

Eric Stein
Environmental Science and Engineering Program
School of Public Health

University of California, Los Angeles
Los Angeles, California 90024

ABSTRACT

An information base was developed on the physicochemical properties and transport parameters of mercury, which can be used to predict abiotic and biotic transfer of mercury among environmental media (i.e., air, water, soil, and the biosphere) with emphasis on human exposure pathways. Such information should be useful in the multipathway exposure component of health risk assessment for mercury. The environmental literature relevant to mercury was critically reviewed to: (1) determine the intermedia transfer factors relevant to mercury; (2) evaluate measured values; and (3) recommend estimation techniques applicable to mercury (and homologous compounds) for use in the absence of measured values.

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1.0 INTRODUCTION AND BACKGROUND

1.1 Overview

The assessment of health risk requires the determination of exposure of the human receptor to pollutants from multiple pathways. The movement of chemicals throughout the environment is particularly important to the overall assessment of the exposure to toxic air pollutants since airborne pollutants can be deposited to the soil and water, and can be accumulated in plants and animals. Determination of air toxic contaminant concentrations can be obtained by either pollutant transport modeling or field measurements. Both approaches require an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants through environmental media.

Risk assessment is often accompanied by uncertainties which arise from the lack of data in various areas leading to reliance on assumptions and default values. For example, the assumptions and default values listed in the CAPCOA guidelines (1992) are designed to err on the side of human health protection to avoid underestimating risk to the public. Major sources of uncertainty in multimedia risk analysis for toxic air pollutants include:

- Extrapolation of toxicity data in animals to humans;
- Air dispersion modeling;
- Estimation of emissions; and
- Analysis of multimedia exposure.

This study addresses the final major source of uncertainty listed above, analysis of multimedia exposure.

By identifying the input parameters most critical to multimedia analysis and critically evaluating measured values and estimation techniques, this report should help characterize and minimize the uncertainty associated with estimating risk from multimedia exposure to mercury. However, given the complex behavior of mercury and its compounds in the environment, it is imperative to first review the intermedia transport and transformation processes that affect the distribution of mercury in the environment. As part of this review, intermedia transfer factors for mercury compounds are described in Sections 3 - 7. A summary of representative values and estimation methods for intermedia transfer factors for elemental mercury is given in Table 1-1. The values listed are typically applicable for specific environmental conditions. Discussions of available parameter values and estimation methods are provided, as indicated in Table 4-4.

1.1 Mercury Compounds

Mercury is among the group of elements known as the transition metals. It occupies Group IIB in the Periodic Table, yet it has unusual physical and chemical properties that distinguish it from the other transition metals. Mercury is unique among the metals in that it is a heavy, silver-colored liquid at ambient temperature with relatively high vapor pressure for a metal. The combination of mercury's high vapor pressure and its long atmospheric lifetimes are partially responsible for its global distribution (USDHHS, 1992).

Mercury has three valence states (0, +1, +2) and exists in the environment in its elemental form as well as in a variety of inorganic and organic complexes. The main source of mercury is degassing of the hydrosphere and lithosphere. Anthropogenic emissions account for only 10-30% of total emissions (Nriagu, 1979; USDHHS, 1992). Approximately 80% of anthropogenic emissions are to the air, primarily from fossil fuel combustion, mining, smelting, and from solid waste incineration. Another 15% of anthropogenic emissions occur to the land via direct application of fertilizers and fungicides and municipal solid waste, e.g., batteries and thermometers. An additional 5% of emissions occur via direct discharge of commercial effluent to water bodies. Historically much of the regulatory focus for mercury has been on emissions to water (Lindberg, 1986). However, since the majority of mercury is released to the air increased consideration of the behavior of airborne mercury is warranted.

Table 1-1. Summary of Intermedia Transfer Parameters for Mercury(1)

Parameter	Reported Value	Units	Temperature (K)	References	Section in Text
S	2.8×10^{-7}	mol/l	298	USDHHS, 1992	5.1.1
P_{vp}	1.6×10^{-4}	kPa	293	USEPA, 1984	5.1.2
MW	200.6	g/mol	NA	USDHHS, 1992	5.1.3
T_{BP}	630	K	NA	Reid et al., 1987	5.1.4
T_{MP}	234	K	NA	USEPA, 1984	5.1.5
T_C	1765	K	NA	Reid et al., 1987	5.1.6
P_C	1.5×10^{5}	kPa	NA	Reid et al., 1987	5.1.6
ρ	13.5	g/cm^3	293	USEPA, 1984	5.1.7
H	0.29	Dimensionless	293	WHO, 1990	5.2.1
$\log K_{ow}$	5.95	Dimensionless	298	Travis and Blaylock, 1993	5.2.2
K_d(2)	170-4,200	Dimensionless	NR	Miskimmin, 1991	5.2.3
BCF(2)	10,000-100,000(3)	Dimensionless	NR	WHO, 1990	5.2.4
B_{vaw}	490	Dimensionless	298	Travis and Blaylock, 1992	5.2.4.1
D_a	0.70	cm^2/s	NR	Lindberg et al., 1992	See Section 5.3.1
D_w	2.9×10^{-5}	cm^2/s	NR	Fitzgerald, 1989	See Section 5.3.1

Table 1-1. Summary of Intermedia Transfer Parameters for Mercury(1)
(Continued)

Parameter	Reported Value	Units	Temperature (K)	References	Section in Text
Atmospheric Reaction Rate Constants	See Section 6.1.1.1				
V_d	0.006-0.12	cm/s	see Table 6-5 for details		6.1.2
K_l	See Section 5.3.2.2				
K_s	See Section 5.4.2.1				
Rain Washout Coefficient	See Section 6.1.3				
Mercury Accumulation in Soil and Sediment	See Section 6.3				
Mercury Accumulation in Biota	See Section 6.4				

NA = Not Applicable.
NR = Not Reported.

(1) All values are for elemental mercury (Hg^0) unless otherwise indicated.

(2) Value for monomethylmercury.

(3) BCF in top carnivores.

There is conflicting evidence regarding long term changes in anthropogenic mercury emissions. Boutron (1986) studied snow and ice core samples and found no clear trend for changes in mercury concentration over the last 800 years. Conversely, Travis and Blaylock (1993) summarize findings which assert that mercury levels in tree rings as well as in peat, soil, and sediment cores reveal a four to five fold increase in concentration since the beginning of the industrial revolution. They estimate that this translates to an increase of anthropogenic emissions of 1.5% per year in the Northern Hemisphere over the past twenty years. This discrepancy may result from the fact that measurements were made at different times of the year and for varying intervals. Furthermore, identifying spatial and temporal trends is difficult due to different behaviors and half-lives of various species of mercury. To date the data are too sparse to satisfactorily resolve the temporal and spatial variability in mercury source strength (Fitzgerald, 1989).

Distribution of mercury among the various environmental media is determined by the different physical and chemical forms in which mercury occurs. The characteristics and interactions of these species with their surroundings determine the transport, transformations, and removal mechanisms of mercury, e.g., settling to sediments, atmospheric deposition, and volatilization into the atmosphere (Schroeder, 1989). It is interesting to note that it is thought that the most important "sink" for mercury is deposition of HgS to sediments (Andersson et al., 1990).

Mercury is unique among environmental toxicants in that man's input into the environment is of less significance compared to natural sources (WHO, 1990). Furthermore, total global mercury loading appears to be relatively insensitive to increases in anthropogenic emissions (Lindberg et al., 1987). However, human activity influences mercury's behavior in environmental media and thus the global cycle of mercury. For example:

- increase in global temperature may increase volatilization of mercury from soils and water (Andersson et al., 1990).

- increased releases of oxidants into the atmosphere may increase the rate of oxidation of elemental mercury leading to complexation and subsequent deposition of inorganic mercury complexes (Lindberg et al., 1987).

- increased acidity of rain and lakes may increase methylation and associated bioavailability of methylmercury (Iverfeldt and Lindqvist, 1986; Fitzgerald, 1989).

Bioavailability and toxicity of mercury are affected by the speciation of mercury. Although mercury is generally considered one of the most toxic metals (Serpone et al., 1988), the different forms of mercury have differing toxicities associated with them. The main routes of exposure for the general population are through inhalation of elemental mercury and ingestion of food contaminated with methylmercury (with fish consumption being the main concern). Although mercury is toxic, it has not been shown to be carcinogenic (USDHHS, 1992). The main targets for mercury toxicity in humans are the renal and central nervous systems, with fetal nervous systems being especially sensitive (USDHHS, 1992).

2.0 OBJECTIVES

The overall objective of this report is to present information that is pertinent to the prediction of the transfer of mercury between media such as air, water, soil, and biota in order to refine the multipathway exposure component of health risk assessments. The specific objectives were to: (1) critically review the literature to obtain the parameters necessary to determine environmental intermedia transfer factors for mercury; (2) evaluate and update intermedia transfer factors currently used in multipathway exposure assessments; and (3) provide pollutant-specific estimates where default values are now used, or no value is available.

3.0 METHODOLOGY

In this study, a thorough investigation was conducted of the literature values reported for key factors and parameters which govern the partitioning of mercury in the various important environmental compartments and the food chain, following mercury's release to the atmosphere. Whenever possible, the reported values for a given parameter were placed on a common basis of units and conditions, and the parameter values were critically evaluated to determine which of these numerical values appear to be of greatest reliability and utility in conducting multipathway exposure assessments. Where no reliable values are found to be available in the literature or default values are currently being used in such discussions, pollutant specific estimates are provided. The details of the methods used, and the properties and parameters investigated, are discussed below.

3.1 Literature Review

A literature search of Dialog (NTIS, Pollution Abstracts, Enviroline, CAS) and UCLA Orion, Melvyl, and EMS library databases was conducted. The UCLA NCITR library was also reviewed for relevant publications. Through this process, the pertinent physicochemical properties, intermedia transport, and biotransformation of mercury were identified, obtained, reviewed, and summarized. Where no measured parameter values were found in the literature, estimated values were obtained from estimation methods applicable to mercury and the mercury compounds of interest.

3.2 Selection of Parameters

In order to critically review intermedia transfers, a number of input parameters, required in multimedia exposure assessment, were considered. The final selection was based on the chemical and physical interpretation of the input parameters, their applicability to different classes of pollutants, and measures of the environmental consequences of intermedia transfers. Specifically, input parameters from the Air Resources Board/ Department of Health Services (ARB/DHS) Health Risk Assessment (HRA) software and algorithms (CAPCOA Guidelines, 1990, 1991, 1992) and the South Coast Air Quality Management District Multi-Pathway Health Risk Assessment Input Parameters Guidance Document (SCAQMD, 1988) were considered.

3.2.1 Chemical Processes

A review of the literature revealed that the processes that chiefly determine the speciation, transformation and thus, also the transport of mercury in the environment are as follows:

- Microbial methylation and demethylation;
- Oxidation-Reduction (redox) reactions;
- Solubility and precipitation equilibria;
- Uptake by biota;
- Atmospheric dry and wet deposition;
- Volatilization; and
- Sorption and desorption.

3.2.2 Physicochemical Parameters

The physicochemical properties of mercury are needed for the determination of parameters such as partition coefficients and biotransfer factors, as well as for the analysis of intermedia transport parameters (e.g., mass transfer coefficients).

A critical literature review was conducted and it was determined that the minimum necessary physicochemical parameters required for conducting a multimedia exposure assessment of mercury as described by CAPCOA, 1992 and other models (e.g., SMCM, Fugacity, and GEOTOX) are as follows:

- Water Solubility;
- Vapor Pressure;

- Molar Volume;
- Boiling Point; and
- Molecular Weight.

The definition of these parameters and the results of the literature review are presented in Section 5.0.

3.2.3 Partition Coefficients

Mercury released to the environment is distributed to various environmental compartments as a result of transport processes. The net transport of mercury from one compartment to another may be limited by equilibrium constraints and quantified by partition coefficients. Thus, the partition coefficient, H_{ij} is generally defined as

$$H_{ij} = C_i/C_j \qquad (3\text{-}1)$$

where C_i is the equilibrium concentration in compartment i and C_j is the equilibrium concentration in compartment j. The following types of partition coefficients for mercury were considered in this study:

- Henry's Law Constant;
- Octanol-Water Partition Coefficient;
- Soil/Water-Organic Carbon Partition Coefficient; and
- Bioconcentration Factors.

Values for some partition coefficients for mercury reported in the literature have been determined experimentally in simulated ecosystems and estimated for others. These partition coefficients are discussed individually in Section 5.0.

3.2.4 Intermedia Transport Parameters

In order to estimate the rate of mercury transport across environmental phase boundaries, one must first be able to describe the transport mechanisms and consequently estimate the associated transport parameters as a function of the appropriate environmental conditions. Intermedia transport processes occur by either convective transport (not addressed in this report) or interfacial transport from one environmental compartment to another.

Interfacial mass transfer coefficients are required to predict the mass flux of mercury and related compounds across the various interfaces and thus, their accumulation in the environmental medium of interest. The relevant intermedia transfer parameters for mercury are as follows:

- Diffusion Coefficients in Air and Water;
- Intermedia Mass Transfer Coefficients;
- Dry Deposition Velocity;
- Washout Ratios; and
- Biotransfer Factors.

In addition, bioavailability and pharmacokinetics should also be considered in evaluating mercury accumulation in biological receptors.

4.0 SOURCES AND CHEMISTRY OF MERCURY

Mercury is a naturally occurring element found in rocks, soils, water, and volcanic dust. Mercury is ubiquitous in the environment and exists in three valance states (0,+1,+2) as well as in various inorganic and organic complexes. Elemental mercury is the most common form found in nature. Monovalent and divalent forms usually do not exist as ionic species, but are associated with inorganic or organic compounds. Annual global emissions of elemental mercury are on the order of 10^6 kg/yr (Nriagu, 1979; Schroeder et al., 1991;

USDHHS, 1992). The majority of emissions are in the form of elemental mercury which degasses from the lithosphere and hydrosphere. Anthropogenic emissions account for 10-30% of total annual mercury emitted (Nriagu, 1979; USDHHS, 1992).

The main anthropogenic sources of mercury are emissions of elemental mercury to the air. Mercury has a variety of manufacturing and industrial uses. For example, mercury's high surface tension, uniform volume expansion and inability to wet and cling to glass make mercury useful in measuring devices such as barometers and thermometers. Mercury's low electrical resistivity and high thermal conductivity make it a useful coolant. In addition, its ability to form amalgams make it useful for metal recovery and dental fillings. The brilliant hues have led to mercury use in dyes and paints (Nriagu, 1979). Also, the toxicity of mercury to biota led to its widespread use as a bactericide and fungicide. The main sources and uses of mercury are summarized in Table 4-1.

Approximately 85% of anthropogenic mercury emissions are released as by-products of various industrial processes including coal mining, fossil fuel combustion, mercury vapor lights and chloroalkali production (the simultaneous production of chlorine and caustic soda) (Nriagu, 1979; USEPA, 1984; USDHHS, 1992; Lapp et al., 1993). Mercury emissions from smelting, combustion and chloroalkali production are 99% in the gaseous form and 1% in the aerosol form. This distribution between gaseous and particulate forms is not affected by the type or temperature of combustion (Pacyna, 1987).

Mercury vapor emissions from defunct power plants and waste deposits can approach those from operational plants, making them a source of concern for exposure assessments (Lindberg, 1987). Emissions from the soils of non-operating industrial sites are temperature dependent and influenced by vegetative cover. Moreover, plants growing on these contaminated soils may accumulate mercury by root or leaf uptake (Pacyna, 1987).

Table 4-1. Sources and Uses of Mercury

Name	**Form**	**Source or use**
Mercury	Metallic or Elemental	Chlorine-alkali manufacturing Dental fillings Gold mining Electrical equipment (batteries, switches Instruments (thermometers, barometers)
Mercuric mercury	Inorganic (Hg^{+2})	Electrical equipment (batteries, lamps) Skin care products Medicinal products
Mercurous mercury	Inorganic (Hg^{+1})	Electrical equipments (batteries) Medicinal products
Methylmercury	Organic (CH_3Hg^{+1})	Diet (e.g., contaminated fish) Polluted sediment
Phenylmercury	Organic ($C_6H_5Hg^{+1}$)	Fungicides Pigments (paints)

Source: USDHHS, 1992

In the atmosphere, Hg^0 is oxidized by O_3 to Hg^{++} via either gas phase reactions or aqueous phase reactions in clouds and fog (Schroeder et al., 1991). Hg^{++} can complex with other ions, primarily chlorine, to form $HgCl_2$. Mercury deposits to water and soil where it is oxidized to Hg^{++}. Once oxidized, divalent mercury is methylated by microbes to methylmercury compounds. Monomethylmercury is absorbed by aquatic plants and animals and bioconcentrates up the food chain. Dimethylmercury volatilizes to the air where it photolyses to methane and elemental mercury or is oxidized by the hydroxyl radical. In anaerobic environments and in the presence of complexing agents, mercury sulfide may form, which precipitates and deposits onto sediments. Although the sediments are considered as sinks for HgS, some HgS can be resolubilized by bacterial transformation. In general, flux of mercury from the water and soil back into the air exceeds deposition (Lindberg et al., 1991); therefore, the atmosphere acts as a minor sink for mercury. An overview of the global mercury cycle as proposed by Nriagu (1979) is presented in Figure 4.1.

In the atmosphere, mercury consists primarily of four chemical forms: elemental mercury (Hg^0), mercuric chloride ($HgCl_2$), monomethylmercury chloride (CH_3HgCl), and dimethylmercury ($(CH_3)_2Hg$) (Schroeder et al., 1991). The toxic manifestations of mercury exposure appear to be determined by the bioavailability and biochemical interactions of monomethyl and dimethylmercury as well as by elemental mercury. It is therefore necessary to selectively determine the amounts of these mercury compounds rather than an assortment of other mercury compounds in a variety of environmental matrices. The U.S. Department of Health and Human Services (USDHHS, 1992) determined that these three mercury compounds are emitted to the air and present the greatest known exposure and health risk. Therefore, this report focuses on these mercury compounds.

The important reactions or processes controlling the distribution of mercury compounds in environmental systems are methylation/demethylation, redox, precipitation/dissolution, and sorption/desorption (Bodek et al., 1988). Although these processes are complex and interrelated, each must be considered in order to predict concentrations, mobility, and toxicity of mercury in the environment. The general chemistry of these

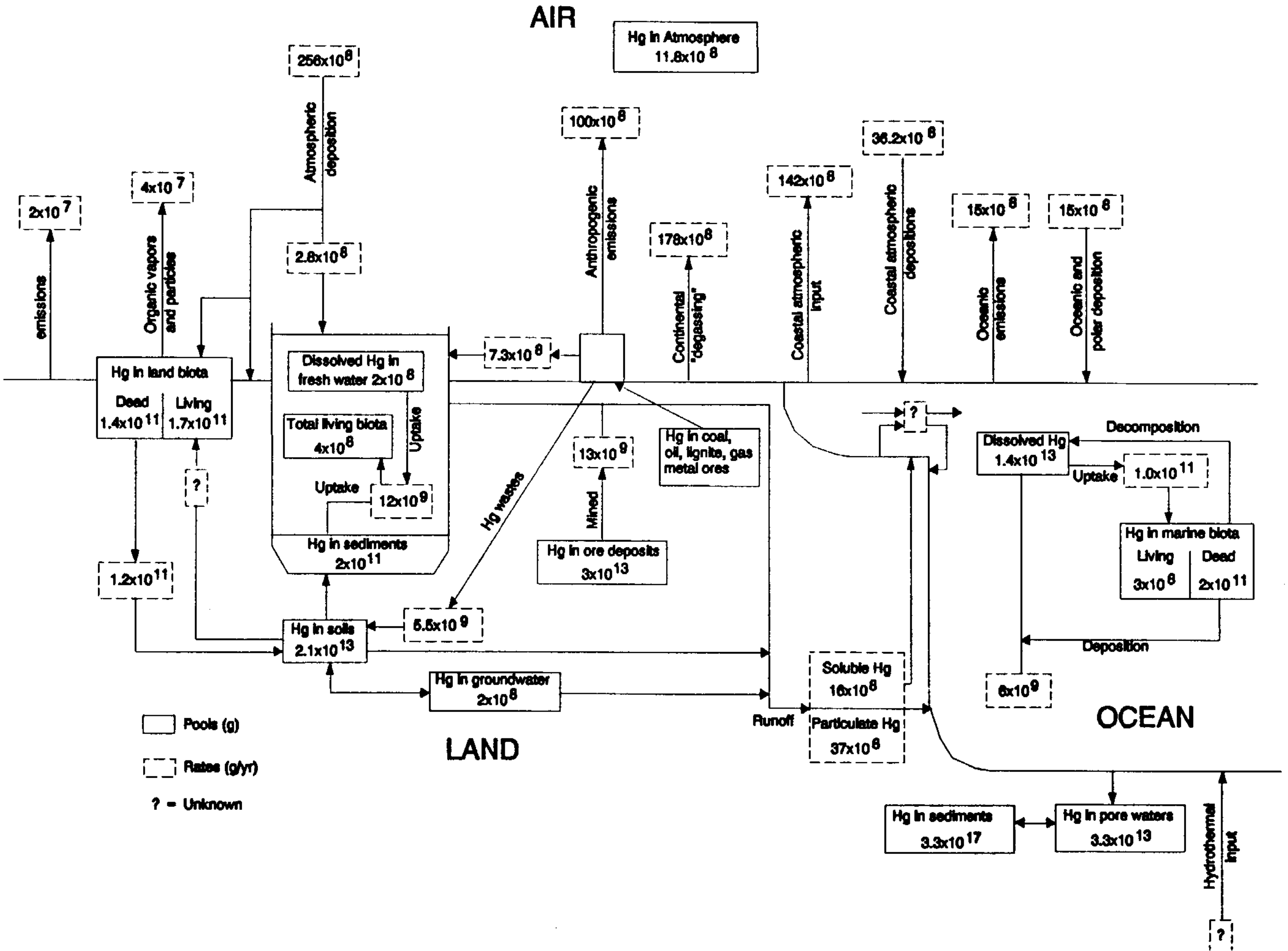

AIR
Hg in Atmosphere 11.8x10^{8}
2x10^{7}
emissions
4x10^{7}
Organic vapors and particles
256x10^{8}
Atmospheric deposition
2.8x10^{8}
100x10^{8}
Anthropogenic emissions
178x10^{8}
Continental "degassing"
142x10^{8}
Coastal atmospheric input
36.2x10^{8}
Coastal atmospheric depositions
15x10^{8}
Oceanic emissions
15x10^{8}
Oceanic and polar deposition
Hg in land biota
Dead 1.4x10^{11}
Living 1.7x10^{11}
?
1.2x10^{11}
Dissolved Hg in fresh water 2x10^{8}
Total living biota 4x10^{8}
Uptake
Uptake
12x10^{9}
Hg in sediments 2x10^{11}
7.3x10^{8}
13x10^{9}
Mined
Hg in coal, oil, lignite, gas metal ores
Hg in ore deposits 3x10^{13}
Hg wastes
5.5x10^{9}
Hg in soils 2.1x10^{13}
Hg in groundwater 2x10^{8}
Runoff
Soluble Hg 16x10^{8}
Particulate Hg 37x10^{8}
?
Dissolved Hg 1.4x10^{13}
Decomposition
Uptake
1.0x10^{11}
Hg in marine biota
Living 3x10^{8}
Dead 2x10^{11}
Deposition
6x10^{9}
OCEAN
LAND
Hg in sediments 3.3x10^{17}
Hg in pore waters 3.3x10^{13}
Hydrothermal input
?
Pools (g)
Rates (g/yr)
? = Unknown

Figure 4-1. Present-day global cycle of mercury (Nriagu, 1979).

reactions are discussed in the context of mercury compounds in the following subsections. The implications of these reactions for distribution of mercury in environmental media are discussed in Section 6.0.

4.1 Microbial Methylation and Demethylation

Elemental mercury which is deposited from the air to the water or soil can be modified by microorganisms. The main transformations which occur are oxidation/reduction (see Section 4.2) and methylation/demethylation. These reactions can produce mercury species with higher mobility, solubility and toxicity. Methylation of mercury by microorganisms acts as a detoxification mechanism for the microbe; however, the methylated products can have higher bioavailability and toxicity to plants and animals.

Mercury must be oxidized to the divalent form in order for methylation to occur. Methylation occurs on surficial sediments and soil and can be influenced by a variety of environmental factors (see Table 4-2; Moore, 1991). Mercury can be methylated by anaerobic, and to a lesser extent aerobic, microbes to form either mono- or di-methylmercury, as shown in the reactions below:

$$Hg^{+2} + RCH_3 \rightarrow CH_3Hg^+ + R^\bullet \tag{4-1}$$

$$2CH_3Hg^+ + H_2S \rightarrow (CH_3)_2Hg + HgS + 2H^+ \tag{4-2}$$

The relative proportion of mono- and di- methylmercury formed is dependent on the mercury concentration and the pH of the system. Monomethylmercury (Reaction 4-1) formation is favored under acidic conditions when mercury concentrations are relatively high. Dimethylmercury formation (Reaction 4-2) is favored under neutral or alkaline conditions when mercury concentrations are low, and in the presence of a strong complexing agents (such as H_2S) (see Figure 4.2; Nriagu, 1979). The rate of synthesis of monomethylmercury is about 6000 times faster than dimethylmercury; therefore, in most environmental systems only 3% of methylmercury is in the dimethyl form (Regnell, 1990).

Table 4-2. Factors Influencing the Rate of Methylation (ROM) of Inorganic Mercury

Factor	Response
Temperature	Increases ROM to a maximum at 35°C
Sulfide content of sediment	Decreases ROM at sulfide levels of 0.9-7.1 mg/g dry weight of sediment
Dissolved oxygen	Decreases ROM with increasing oxygenation
Organic content of sediment	Increases ROM with increasing nitrogen content of sediment
Chloride content of sediment and water	Decreases ROM under estuarine conditions
pH	Increases ROM with decreasing pH

Source: Moore, 1991

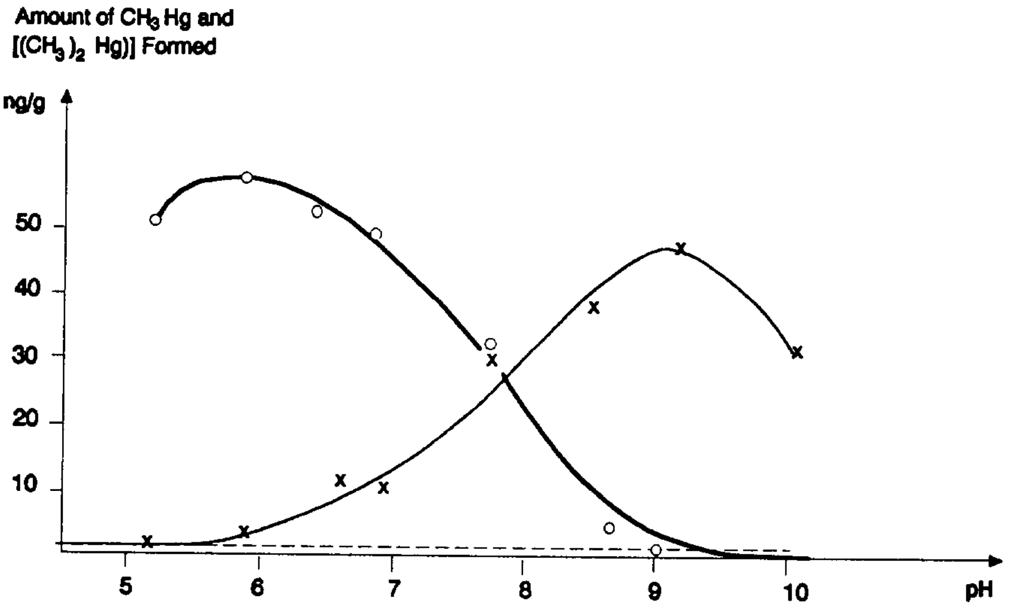


Figure 4-2. Formation of mono- and dimethylmercury in organic sediments at different pH during a 2-week incubation period. Total Hg concentration 100 mg/kg.

o - CH_3Hg^{+1} in water and sediment.

x - Volatile $(CH_3)_2Hg$ trapped in Hg^{2+} after aeration.

Source: Nriagu, 1979.

Methylation can result in re-mobilization of sorbed or precipitated mercury. Monomethylmercury is kinetically inert toward decomposition and is soluble and, thus, is bioavailable for uptake by aquatic plants or animals (USDHHS, 1992). Dimethylmercury is volatile and when released to the atmosphere undergoes photolysis forming elemental mercury and two methyl radicals (Bodek et al., 1988)

$$(CH_3)_2Hg \xrightarrow{h\nu} Hg^0 + 2CH_3 \qquad (4\text{-}3)$$

Dimethyl mercury also undergoes oxidation by OH radical displacement reaction forming CH_3HgOH and CH_3.

$$(CH_3)_2Hg + OH = CH_3HgOH + CH_3 \qquad (4\text{-}4)$$

Biological demethylation occurs at a much slower pace than methylation. The process involves hydrolysis of the metal-carbon bond forming Hg^{+2} and methane. Divalent mercury is then reduced to elemental mercury, which permits volatilization.

$$CH_3Hg^+ \rightarrow CH_3^\bullet + Hg^{+2} \qquad (4\text{-}5)$$

$$Hg^{+2} \rightarrow Hg^0 \qquad (4\text{-}6)$$

The biological cycle of mercury is summarized in Figure 4.3 (USEPA, 1979).

4.2 Redox Reaction

A redox reaction consists of two parts or half-reactions. These are the oxidation reaction in which a substance donates electrons and the simultaneous reduction reaction in which a substance accepts electrons. An analogy can be drawn between redox reactions in the hydrosphere and acid-base reactions. The activity of the hydrogen ion, H^+, is used to express the degree to which water is acidic or basic. By analogy, *electron activity* expresses the degree to which water is reducing or oxidizing. Water with high electron activity is said

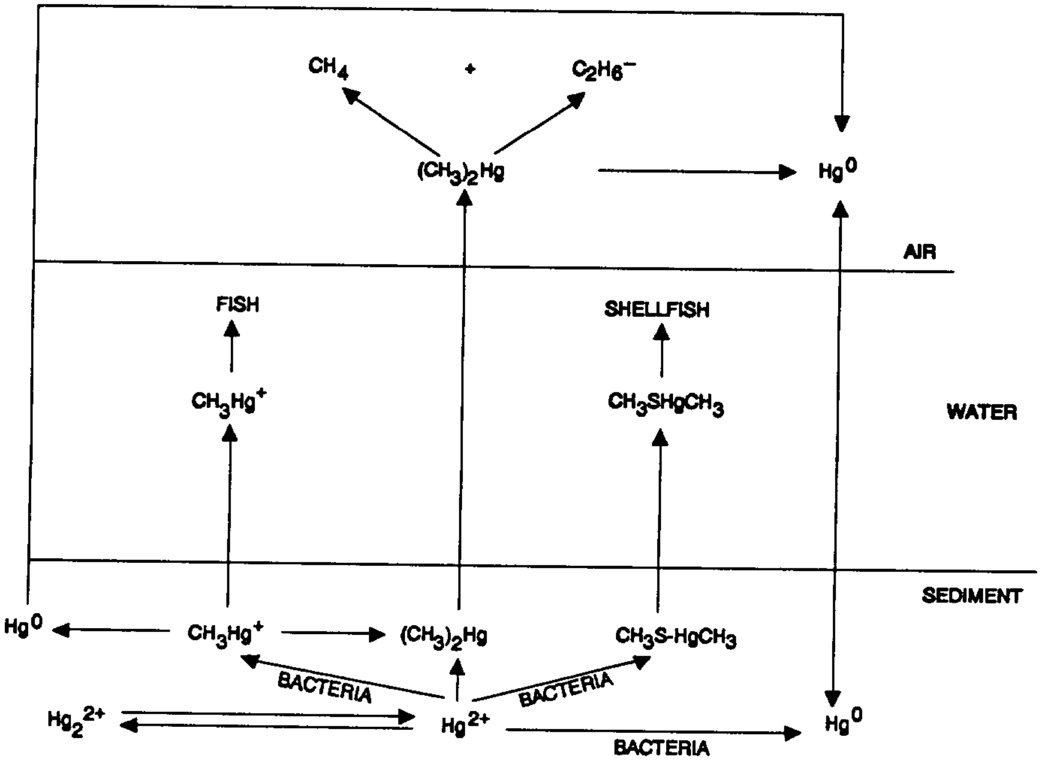

CH4
+
C2H6⁻
(CH3)2Hg
Hg0
AIR
FISH
SHELLFISH
CH3Hg+
CH3SHgCH3
WATER
SEDIMENT
Hg0
CH3Hg+
(CH3)2Hg
CH3S-HgCH3
BACTERIA
BACTERIA
Hg2 2+
Hg2+
Hg0
BACTERIA

Figure 4.3. The biological mercury cycle in the aquatic environment. Source: U.S. EPA, 1979.

to be reducing while water with low electron activity is said to be oxidizing (Manahan, 1991). Just as pH can be defined as

$$pH = -\log(a_{H^+}) \tag{4-7}$$

where a_{H+} is the activity of the hydrogen ion in aqueous solution, the redox intensity factor, pE, is defined as

$$pE = -\log(a_{e^-}) \tag{4-8}$$

where a_{e-} is the activity of the electron in aqueous solution. pE reflects the ratio of electron acceptors (oxidants) to donors (reductants) in a redox couple. High values of pE correspond to strongly oxidizing systems, usually characterized by aerobic environments, whereas low values of pE reflect reducing conditions characteristic of anaerobic environments. Systems near equilibrium should have a small range of pE values while systems far from equilibrium should have a broad range (Scott and Morgan, 1990).

The redox potential (Eh) of the system is an alternative to pE that is equivalent at any specified temperature and equivalent intensity factor (Scott and Morgan, 1990)

$$Eh = E^{\circ}\ (\text{redoxcouple}) + \frac{2.3RT}{nF} \log \frac{[\text{oxid}]}{[\text{red}]} \tag{4-9}$$

where E° is the standard electrode potential, R is the universal gas constant, T is the Kelvin temperature, F is the Faraday constant, and n is the number of electrons stated in the half-reaction. The activity of the oxidant and reductant are represented by [oxid] and [red], respectively. Values of Eh are more often used when experimental data for the electrode potential (E°) for the redox couple are available, whereas pE is convenient to use when equilibrium constant data are available. The range of Eh values in aqueous systems is approximately from -0.8 to +1.2V (Bodek et al., 1988). Figure 4.4 shows theoretical Eh-pH relationships between aqueous mercury species at equilibrium (Hem, 1970, cited by USEPA, 1979).

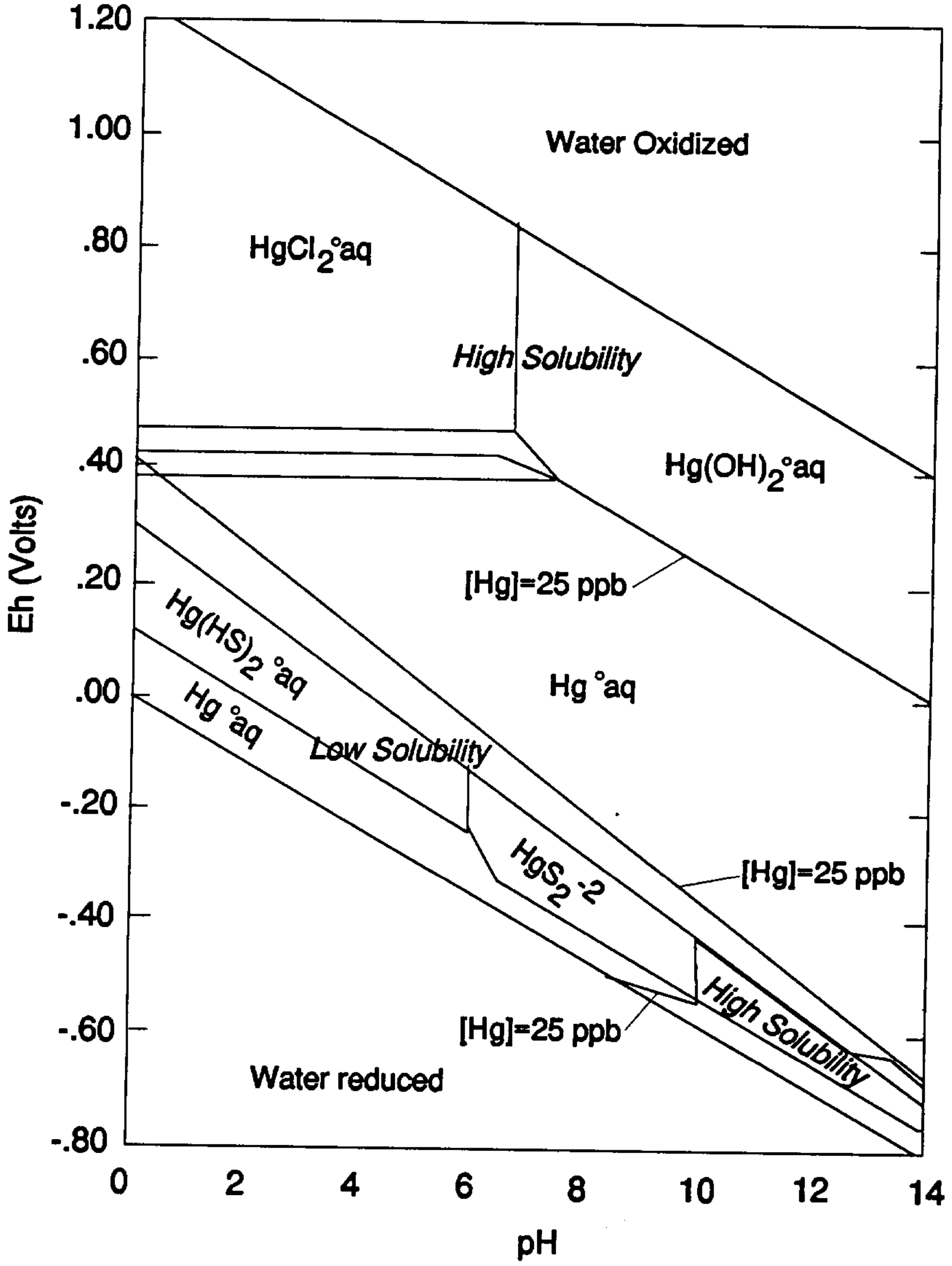


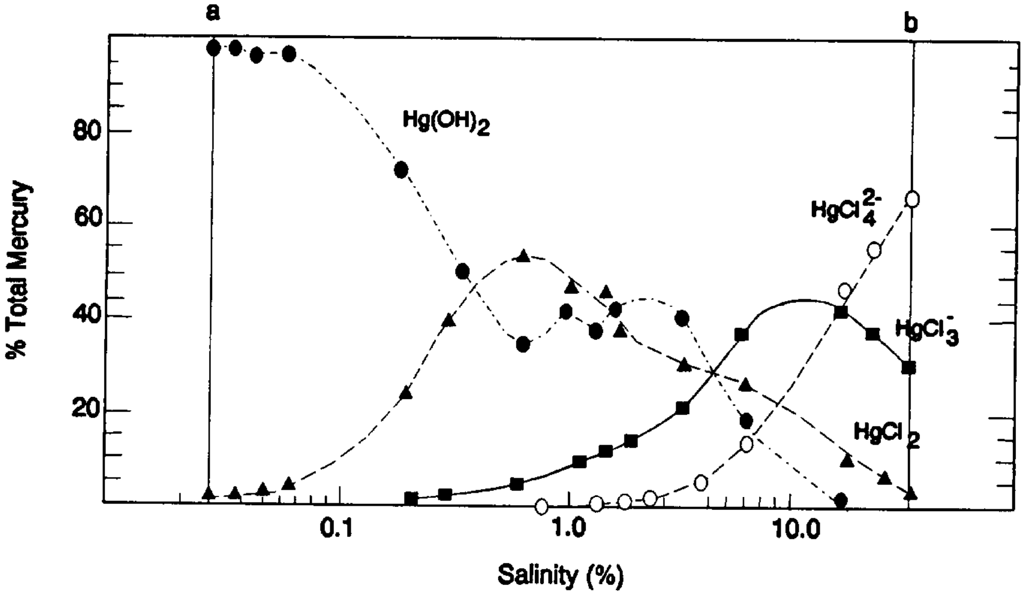
Figure 4.4. Fields of stability for aqueous mercury species at 25°C and 1 atmosphere pressure. Dashed line indicates solubility of mercury. Source: U.S. EPA, 1979.

The redox potential of natural waters is determined by the concentrations of dissolved oxygen and dissolved organic matter. Under acidic conditions ($pH < 6$) elemental mercury can be oxidized to divalent mercury. The environmental behavior of divalent mercury is determined by its subsequent complexation with inorganic and organic compounds (USEPA, 1979). The importance of these oxidation reactions is that divalent mercury is a necessary precursor for the formation of compounds with increased solubility ($HgCl_2$ and $Hg(OH)_2$) and increased bioavailability (CH_3Hg^+). Oxidation may occur in water, soil, and sediments by biotic or abiotic reactions. In contrast, complexation with monovalent mercury typically does not occur due the fact that monovalent mercury is a much weaker acid than divalent mercury (Bodek et al., 1988).

Methylation of divalent mercury results in methylmercury, which is bioavailable and accumulates up the food chain (see Section 4.1). Unlike methylated mercury, inorganic complexes are not associated with bioconcentration. Under oxidizing conditions, divalent mercury forms predominately chloro- and hydroxo- complexes. In freshwater systems $HgCl_2$ and $Hg(OH)_2$ are the dominant mercury species, while $HgCl_4^{-2}$ is the dominant species is saltwater systems (see Figure 4.5) (Nriagu, 1979; Bodek et al., 1988). Under reducing conditions, and in the presence of complexing agents such as H_2S, HgS forms and precipitates. If water is perturbed and re-oxygenated, HgS may be re-solubilized and become available for subsequent oxidation reactions. Formation of inorganic complexes are important in that they can dramatically increase the solubility of mercury (see Section 4.3), resulting in increased mobility. Soluble mercury compounds are subject to oxidation to Hg^{+2} and subsequent methylation, which increases bioavailability (see Section 4.1).

Bacteria and yeast species have been isolated which can reduce Hg^{+2} and $HgCl_2$ to Hg^0 using reduced nicotinamide adenine dinucleotide (NADH) as a coenzyme by the following reaction (Bodek et al., 1988):

$$Hg^{+2} + NADH + H^+ \rightarrow Hg^0 + 2H^+ + NAD^+ \qquad (4\text{-}10)$$



Total mercury concentration = 10^{-9} M
Line 'a' corresponds to fresh water:
Cl^- = 5×10-4 M, pH = 7.19
Line 'b' corresponds to seawater:
Salinity = 36%, pH = 8.29

Figure 4.5. Calculated inorganic speciation of mercury in an estuary as a function of salinity (Bodek et al., 1988). (Note: Salinity (%) is defined as the total grams of dissolved solids per kilogram of seawater.)

The elemental mercury which forms as a result of this reaction can volatilize and reenter the atmosphere.

4.3 Precipitation - Dissolution Reactions

In studies of environmental water quality, it is often necessary to know the solubility of a given solid and whether a solid phase can precipitate from water of a given composition. Such questions can often be resolved through consideration of the chemical equilibria between solids and aqueous solutions. The state of chemical thermodynamic equilibrium reflects two important quantities (Bodek et al., 1988):

(1) The current state of the water, with respect to its ability to dissolve or precipitate certain chemicals; and

(2) The expected change in concentration of dissolved substances, if certain solid phases were to dissolve in, or precipitate from, the water.

Aqueous solubility of Hg^0 and Hg^{+2} are low; at 20°C, the solubility of Hg^0 and Hg^{+2} equals 0.025 ppm and 0.039 ppm, respectively (Bodek et al., 1988). However, the aqueous solubility can increase due to reaction or complexation with inorganic species present in water. For example, Hg^{+2} has a solubility of 0.039 ppm; however, when Hg^{+2} is hydrolized to $Hg(OH)_2$, the solubility increases to 107 ppm (Bodek et al., 1988). Complexation with Cl^- has an even more pronounced effect on solubility. For example, at Cl^- concentrations of 3.5 ppm, solubilities of $Hg(OH)_2$ and HgS increase by factors of 55 and 408, respectively (Bodek et al., 1988).

pH also affects the solubility of mercury and mercury compounds. For example, Trost (1970) (as reported by Bodek et al., 1988) observed a 30 fold increase in the solubility of HgS between a pH of 2 and 5. Mercury compounds readily bind to the surface of dissolved organic carbon (see Section 4.4); therefore, solubility of mercury will increase in water with high concentrations of humic or fulvic acids (Trost, 1970 as reported by Bodek et al., 1988). Under aerobic conditions, the most common insoluble species present is Hg^{o}, which can volatilize out of the water (Bodek et al., 1988). Under anaerobic conditions HgS is the most common insoluble species present (solubility = 10^{-53} ppm; Bodek et al, 1988). HgS tends to precipitate into sediments and is rapidly lost from the free water column (see Section 4.4).

4.4 Sorption-Desorption

An understanding of sorption and attenuation is necessary to assess the fate of inorganic compounds in the environment. Sorption refers to the removal of solute from the aqueous phase of an environmental system at the surface of a solid phase. The bioavailabilities of dissolved versus sorbed, insoluble species also differ; dissolved species being more available for uptake by both plants and animals (Bodek et al., 1988).

Divalent mercury forms strong complexes with organic ligands. The binding affinity between mercury and organic compounds can be quantified with a conditional stability constant. The conditional stability constant is the logarithm of the overall formation constant for the cumulative binding of a ligand to a central metal cation under specific conditions (e.g., ligand and metal concentrations, salinity, temperature, and pH). The conditional stability constant (K_0) can be represented by the following equation (Dean, 1985):

$$K_0 = \frac{[\text{organometalic complex}]}{[\mathrm{Hg}^{e}]\ [\text{humic acid}]} \qquad (4\text{-}11)$$

The stability constant for Hg^{+2}-humic complexes range from 18.4-21.1, depending on conditions. In comparison, stability constant for other metal-organic complexes range from less than one to the high twenties. Formation of mercury-humic complexes increase the solubility, mobility, and bioavailability of mercury. In seawater, competition from high Cl^{-} concentrations causes a decrease in the proportion of Hg^{+2} bound with humics with increasing salinity (Bodek et al., 1988).

Sorption onto soils and sediments can act as a dominant removal mechanism for mercury from solution. Reimers and Krenkel (1974) (as reported by Bodek et al., 1988) report that sorption increases with increasing organic carbon content. The magnitude of the effect of pH on sorption differs for different species of mercury. At $pH < 5$ optimal sorption of $HgCl_2$ to organics occurs. At $pH > 5$ formation of soluble Hg-humate complexes decreases sorption (Bodek et al., 1988). Therefore, the pH of aquatic systems influences the concentrations of dissolved, and therefore bioavailable, mercury complexes.

Desorption rates are slow, ranging from 10^{-3} to 10^{-5} times the rate of sorption. Desorption of Hg^{+2} from river sediments was found to be less than 1% after 70 hours of agitation with distilled water (Bodek et al., 1988). However, dredging or oxygenating sediments may resolubilize precipitated forms of mercury allowing for oxidation and subsequent methylation of mercury.

Adsorption of mercury to soil and sediment can be represented using the Langmuir isotherm:

$$S = \frac{(K_L A_m C)}{(1 + K_L C)} \quad , \quad \mu \text{ mol/g} \tag{4-12}$$

where S = μ moles of Hg^0 sorbed at equilibrium per gram of solids;
K_L = sorption constants (related to the binding affinity);
C = total concentration of Hg^0 in solution at equilibrium (molality); and
A_m = maximum sorption capacity of solid (mass of adsorbed Hg^0 required to saturate a unit of mass of solid).

In all cases, "solid" can refer to either soils or sediments. Langmuir constants, which represent binding affinities and adsorption equilibrium, for mercury sorption onto soils and sediments are given in Table 4-3.

Table 4-3. Langmuir Constants for Elemental Mercury Sorption onto Soils and Sediments

	% Organic Carbon	**% Clay**	**Particle Size (mm)**	**A_m (μmol/g)**	**Log K_L (log M^{-1})$^{(a)}$**
Soils					
Asquith	0.79	8.8	--	1.6	--
Oxbow	2.98	45.5	--	12.3	--
Sediments	**% Organic Matter**				
	10.78		0.35	463.6	5.9
	1.81	--	0.225	448.7	4.8
	0.42	--	0.240	349.0	4.2
	0.57	--	0.260	219.4	4.3

Source: Bodek et al., 1988

(a) M = Molality (mol/kg)

4.5 Analysis of Mercury in Environmental Media

The environmental processes which affect the fate of mercury in the environment are summarized in Table 4-4. The focus is on the behavior of the mercury species which are of greatest concern for health risk assessments, namely, elemental mercury, monomethylmercury, and dimethylmercury.

5.0 PHYSICOCHEMICAL PROPERTIES OF MERCURY

The following subsections define, discuss, and summarize the findings of the literature search for each of the parameters reviewed in this study. Equations defining input parameters and estimation techniques are presented, where appropriate.

The species of mercury which present the greatest risk for environmental toxicity are elemental mercury and methylmercury. Therefore, values found in the literature for these compounds are emphasized throughout Sections 5.1 through 5.3. Data in the tables are arranged by decreasing order of reliability. Measured values of known uncertainty are considered the most reliable and are thus listed first. Measured values reported without estimates of uncertainty are listed next, followed by calculated values reported with the corresponding prediction equations and uncertainty estimates. Calculated values reported without their associated estimation equations are reported last.

Values for input parameters have been converted to consistent SI units to facilitate comparison of results. The converted values have been reported with same number of significant figures as the values reported in the corresponding reference. Specific conversion equations are shown in the tables. It should be noted that commonly used forms of estimation equations often require input parameters in non-SI units. These cases have been identified in the text following presentation of the appropriate equations.

Table 4-4. Summary of Aquatic Fate of Mercury

Environmental Process	Summary Statement
Photolysis[a]	Important in the breakdown of airborne mercury complexes, might be important in some aquatic environments.
Chemical Speciation[a]	Controls volatility of metallic mercury by conversion to complexed species. In reducing sediments, HgS will precipitate and may constitute a major chemical sink.
Volatilization[a]	Important to the movement of mercury compounds in and out of the aquatic environment.
Sorption[a]	Sorption processes result in the strong partitioning of mercury into suspended and bed sediments. Sorption is strongest onto organic materials.
Bioaccumulation[a]	Bioaccumulation has been proven to occur via numerous mechanisms. Most are connected to methylated forms of mercury.
Biotransformation[a]	Mercury can be metabolized by bacteria to methyl and dimethyl forms which are quite mobile in the environment.

---

[a] All noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate (U.S. EPA, 1979).

5.1 Physicochemical Parameters for Mercury

Section 3.2 describes the general need for using physicochemical parameters in multipathway assessment. This section also defines and discusses the specific physicochemical parameters that are needed for multimedia analysis of mercury in the environment.

5.1.1 Solubility in Water

The water solubility (S) of a chemical is defined as the maximum amount of the chemical that will dissolve in pure water at a specific pressure, temperature and pH. The units of aqueous solubility are usually stated in terms of weight per weight (ppm, ppb, g/kg, etc.) or weight per volume (mg/L, μg/L, mol/L etc.). Less common units are mole fraction and molal concentration (moles per kg of solvent). In this report solubility is given in mol/L to be consistent with SI units. Values for the water solubility of Hg^0 and HgS found in the literature are summarized in Table 5-1. Since solubility varies with temperature and pH, assessment of the consistency of results reported at different temperatures is difficult. Figure 4.4 illustrates the relationship between pH and solubility of several mercury species.

5.1.2 Vapor Pressure

The saturation vapor pressure, P_{VP}, is a measure of the volatility of a chemical in its pure state and is an important determinant of the rate of vaporization. Estimating P_{VP} requires information on the following properties: (1) critical temperature; (2) critical pressure; and (3) heat of vaporization, and/or the vapor pressure at some reference temperature. The units of P_{VP} can be stated in atm, torr, mm Hg, or Pa. In this report P_{VP} is given in kPa.

Table 5-1. Solubility of Mercury in Water

Species	Solubility (mol/l)	Temperature (K)	Reference
Hg^0	3.19×10^{-7}	293	Samemasa, 1975
Hg^0	2.79×10^{-7}	298	USDHHS, 1992
Hg^0	2.8×10^{-7}	298	Lapp et al., 1993
Hg^0	4.05×10^{-7}	303	USEPA, 1984
Hg^0	1.0×10^{-7}	NR	WHO, 1990
$HgCl_2$	0.33	293	Trakhtenberg, 1974

NR = Not Reported.

The vapor pressure of mercury is dependent on temperature and it can be calculated from the following equation (Reid et al., 1987):

$$\log_{10} P_{vp} = \frac{-0.05223\ A}{T} + B \tag{5-1}$$

where P_{vp} is the vapor pressure (mm Hg), T is temperature (K), and A and B are constants of the Antoine Equation (Eq. 5-1) for elemental mercury given as (Weast and Astle, 1981):

A = 73,000
B = 10.383

Eq. 5-1 is applicable for a temperature range of 193K to 312K and examples of reported values for the vapor pressure of Hg^0 and CH_3HgCl are summarized in Table 5-2.

5.1.3 Molar Volume

The molar volume (V_b) of mercury, expressed in units of L/mol, is the volume of a mole of liquid mercury at the normal boiling temperature. The molar volume of an organic liquid is a useful parameter because it has been correlated with the normal boiling point and it is used in techniques for estimating diffusion coefficients in air and water. Estimated molar volumes of various mercury compounds are presented in Table 5-3.

5.1.4 Molecular Weight

The molecular weight is used for converting from mass to concentration and in various correlations of transport properties (e.g., diffusion coefficients). Table 5-4 presents examples of molecular weight from the literature for various mercury compounds.

Table 5-2. Vapor Pressure of Mercury

Species	Vapor Pressure (kPa)	Temperature (K)	Reference
Hg^0	1.59×10^{-4}	293	Weast and Astle, 1981
Hg^0	1.59×10^{-4}	293	USEPA, 1984
Hg^0	1.59×10^{-4}	293	Trakhtenberg, 1974
Hg^0	1.60×10^{-4}	293	WHO, 1990
Hg^0	2.39×10^{-4}	298	USEPA, 1984
Hg^0	2.66×10^{-4}	298	Lapp et al., 1993
Hg^0	2.50×10^{-4}	298	Schroeder et al., 1991
Hg^0	2.67×10^{-4}	298	Travis and Blaylock, 1993
Hg^0	2.66×10^{-4}	298	USDHHS, 1992
CH_3HgCl	1.13×10^{-3}	293	WHO, 1990

Table 5-3. Molar Volume of Mercury

Species	**Molar Volume (L/mol)**	**Reference**
Hg^0	0.0149	USDHHS, 1992
$HgCl_2$	0.0499	Weast and Astle, 1981
CH_3HgCl	0.0618	Weast and Astle, 1981
$(CH_3)_2Hg$	0.0752	Weast and Astle, 1981

Table 5-4. Molecular Weight of Mercury Compounds

Species	Molecular Weight (g/mol)	Reference
Hg^0	200.6	USDHHS, 1992
$HgCl_2$	271.5	Weast and Astle, 1981
CH_3HgCl	251.1	Weast and Astle, 1981
$(CH_3)_2Hg$	230.7	Weast and Astle, 1981

5.1.5 Boiling Point Temperature

The boiling point temperature, T_{BP}, is defined as the temperature at which the vapor pressure of a liquid is equal to the total pressure above the liquid. For pure compounds, the normal T_{BP} is defined as the T_{BP} at one standard atmosphere of pressure on the liquid. T_{BP} provides an indication of the physical state and volatility of a chemical. T_{BP} is also an important parameter used in the prediction of other physical properties. The normal T_{BP} is easily measured.

Examples of boiling points reported in the literature for Hg^0, $HgCl_2$, and $(CH_3)_2Hg$ are listed in Table 5-5.

5.1.6 Melting Point Temperature

The melting point of a pure substance is defined as the temperature at which its crystals are in equilibrium with the liquid phase at atmospheric pressure. T_{mp} provides an indication of the physical state of a chemical, at the temperature of interest, and can also be used in the prediction of other physicochemical properties, such as vapor pressure and K_{ow}. At well defined temperatures, the melting point is identical to the freezing point.

Examples of melting points reported in the literature for mercury are listed in Table 5-6.

5.1.7 Critical Temperature and Pressure

The critical temperature of a pure substance is defined as the temperature above which a gas cannot be liquified (i.e., a state where there is no distinction between gas and liquid phases). The critical pressure of a pure substance is defined as the minimum pressure required to liquify a gas at its critical temperature. T_c and P_c are parameters often used in estimation of physicochemical parameters such as boiling point, liquid density, vapor pressure, and heat of vaporization.

Table 5-5. Boiling Point of Mercury*

Species	Boiling Point (K)	Reference
Hg^0	629.72	USDHHS, 1992
Hg^0	629.9	Lapp et al., 1993
Hg^0	630.25	Trakhtenberg, 1974
Hg^0	629	USEPA, 1984
Hg^0	630	Reid et al., 1987
Hg^0	629	Schroeder et al., 1991
$HgCl_2$	576	Trakhtenberg, 1974
$HgCl_2$	575	Weast and Astle, 1981
$(CH_3)_2Hg$	369	Weast and Astle, 1981

* Listed order is by decreasing confidence in reported values for each species (see Section 3.0).

Table 5-6. Melting Point of Mercury*

Species	Melting Point (K)	References
Hg^0	234.13	USDHHS, 1992
Hg^0	234.13	Lapp et al., 1993
Hg^0	234.1	USEPA, 1984
Hg^0	234.3	Reid et al., 1987
Hg^0	234.2	Schroeder et al., 1991
Hg^0	234.11	Trakhtenberg, 1974
$HgCl_2$	550	Trakhtenberg, 1974
$HgCl_2$	549	Weast and Astle, 1981
CH_3HgCl	443	USDHHS, 1992
CH_3HgCl	443	Weast and Astle, 1981

* Listed order is by decreasing confidence in reported values for a given species (see Section 3.0).

The critical temperature of elemental mercury is 1765 K and the critical pressure of elemental mercury is 1.5×10^5 kPa (Reid et al., 1987).

5.1.8 Liquid Density

The liquid density (ρ) of a substance is the ratio of its mass to its volume, with units of g/ml. The density varies with molecular weight, molecular interactions, and temperature. Density can be used to calculate molar volume, with units of l/mol, and is a useful parameter in correlations used to estimate diffusion coefficients in air and water.

Examples of densities reported in the literature for mercury and mercury compounds are listed in Table 5-7.

5.2 Partition Coefficients for Mercury

Section 3.2.3 provides general equations for the various partition coefficients. The definition and reported individual partition coefficients are presented in the following subsections.

5.2.1 Henry's Law Constant

The Henry's Law constant is a particularly important parameter for evaluating chemical partitioning between air and water and is required as an input parameter in most multimedia models. The Henry's Law constant of a chemical (H_i) is defined as:

$$H_i = P_i/C_i \tag{5-2a}$$

where P_i is the partial pressure of the compound (e.g., Pascals), at the system temperature, and C_i is the concentration (e.g., mol/m^3) of the chemical in the aqueous phase in equilibrium with the air phase. The dimensionless form of the Henry's law constant is defined as

Table 5-7. Liquid Density of Mercury*

Species	Liquid Density (g/ml)	Temperature (K)	Reference
Hg^0	13.546	293	Lapp et al., 1993
Hg^0	13.456	293	USEPA, 1984
Hg^0	13.594	293	Reid et al., 1987
Hg^0	13.55	293	Schroeder et al., 1991
Hg^0	13.534	298	USDHHS, 1992
$HgCl_2$	5.44	293	Trakhtenberg, 1974
$HgCl_2$	5.44	NR	Weast and Astle, 1981
CH_3HgCl	4.063	NR	Weast and Astle, 1981
CH_3HgCl	4.063	NR	USDHHS, 1992
$(CH_3)_2Hg$	3.069	NR	Weast and Astle, 1981

* Listed order is by decreasing confidence in reported values for a given species (see Section 3.0).

$$H'_i = H_i/RT \tag{5-2b}$$

in which R is the universal gas constant and T is the absolute temperature.

The Henry's Law constant may be determined experimentally or estimated, although it is preferable to use an experimentally determined value. An estimated value of H_i can be obtained by using the saturation vapor pressure and solubility data in the following equation (Lyman et al., 1990; Reid et al., 1987):

$$H_i = P_{vp} /S \tag{5-3}$$

where P_{vp} is the saturation vapor pressure (e.g., Pa) and S is the solubility (e.g., mol/m^3). This expression is valid only for solutes for which the activity coefficient is constant at concentrations ranging from the solubility limit and below.

Examples of Henry's Law constant for various mercury compounds reported in the literature are listed in Table 5-8.

5.2.2 Octanol-Water Partition Coefficient

The octanol-water partition coefficient, K_{ow}, is defined as the equilibrium ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system by the following equation:

$$K_{ow} = C_o/C_w \tag{5-4}$$

where C_o is the concentration in octanol phase and C_w is the concentration in aqueous phase. K_{ow} is dimensionless when the concentrations of C_o and C_w are in the same units (e.g., mol/cm^3). K_{ow} is an important parameter used in the assessment of environmental fate and transport for chemicals because the octanol phase is a surrogate for the lipid phase or

Table 5-8. Henry's Law Constants for Mercury

Species	H (dimensionless)	Temperature (K)	Reference
Hg^0	0.29	293	WHO, 1990
Hg^0	0.18	278	Schroeder et al., 1991
Hg^0	0.37	298	Iverfeldt and Lindqvist, 1984
$HgCl_2$	1.2×10^{-8}	283	WHO, 1990
$HgCl_2$	2.9×10^{-8}	298	Iverfeldt and Lindqvist, 1984
CH_3HgCl	1.9×10^{-5}	298	Iverfeldt and Lindqvist, 1984
CH_3HgCl	1.6×10^{-5}	288	WHO, 1990
$(CH_3)_2Hg$	0.15	273	WHO, 1990
$(CH_3)_2Hg$	0.19	293	Wasik, 1978
$(CH_3)_2Hg$	0.31	298	Iverfeldt and Lindqvist, 1984

organic carbon content of environmental compartments. K_{ow} is considered as one of the most important physicochemical characteristics related to sorption on soil and sediments and bioaccumulation. Since K_{ow} has been correlated to water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life (Lyman et al., 1990), it is a key variable used in the estimation of these properties. Although K_{ow} is expected to vary with temperature and pH, its temperature dependence is rarely reported. The reported log K_{ow} is 5.95 (Travis and Blaylock, 1993) for Hg^0 at 298K and is 2.28 for $(CH_3)_2Hg$ at 298K (Wasik, 1978).

5.2.3 Soil/Water Partition Coefficient

The soil/water partition coefficient (K_d) is a measure of the tendency for compounds to adsorb onto the soil (or sediment) and is defined as the ratio of the amount (mass) of a chemical adsorbed per unit mass of soil or sediment to the concentration of the chemical in the water at equilibrium,

$$K_d = \frac{\text{mg chemical adsorbed/kg soil or sediment)}}{\text{(mg chemical dissolved/liter of solution)}} \tag{5-5}$$

Miskimmin (1991) reported a K_d value for methylmercury of 170 for sand, 760 for silt, and 4,200 for woodchips. The adsorption of elemental mercury is described by the Langmuir isotherm as given in Section 4.4.

5.2.4 Bioconcentration Factors

The traditional measure of a chemical's potential to accumulate in an organism is the bioconcentration factor (BCF), which is defined as a chemical's wet-weight concentration in an organism or tissue divided by its concentration in the medium through which exposure occurs by direct contact (e.g., water for aquatic organisms, or air for terrestrial organisms). The concept of BCF addresses partitioning of a chemical into an organism by non-food routes. Specifically, BCF is defined as:

$$\mathrm{BCF} = \frac{\text{(equilibrium concentration of chemical in receptor)}}{\begin{array}{c}\text{(mean concentration of chemical in the medium}\\ \text{through which exposure occurs by direct contact)}\end{array}} \qquad (5\text{-}6)$$

It is convenient to use the same units for both the numerator and denominator which results in a dimensionless BCF. The term BCF is used with the assumption that uptake across external membranes from the media with which the receptor is in direct contact is the chief pathway for chemical uptake by the organism. It is important to note that BCF values are compound-specific, medium-specific, and species-specific, and experimental data should be used whenever possible. The form of mercury which is most readily absorbed and bioconcentrated is methylmercury. Measured BCF values for methylmercury range from 10,000 to 100,000 for top carnivores (WHO, 1990; USDHHS, 1992; Constantinou et al., 1993).

5.2.4.1 Bioconcentration of Mercury in Vegetation

The concept of BCFs can also be applied to accumulation of mercury in vegetation. Plant accumulation of mercury can involve several different mechanisms, including: (1) root adsorption, (2) root uptake followed by transpirational translocation of mercury from roots to shoots, (3) volatility of mercury from soils and hydroponic solutions followed by foliar adsorption, (4) contamination of plant foliage by mercury laden soil, and (5) atmospheric deposition and leaf-uptake of vapor phase mercury. Trapp et al. (1990) suggested that root uptake and translocation of chemicals with high K_{ow}, such as mercury, in the transpiration stream is not a significant plant contamination mechanism due to their adsorption to organic soils. The study of Bacci et al. (1990) suggests that above ground portions of vegetation are thought to be principally impacted by vapor phase transfers. Also, according to Schroeder et al. (1991), only a negligible fraction of mercury is expected to sorb to particles in the atmosphere as its primary states are gaseous and dissolved forms. The above studies appear to imply that contamination of plants by direct deposition of particles onto which mercury is adsorbed is a negligible exposure pathway. However, volatilization from contaminated soil could be an important transport mechanism that can result in significant quantities of airborne mercury being adsorbed by plant shoots (Lindberg, 1986).

Root Bioconcentration Factor

The concentration of mercury in vegetation due to root uptake, C_{vr}, (e.g., µg/kg fresh plant) has been estimated using the following equation (Travis and Blaylock, 1992):

$$C_{vr} = C_s \cdot B_{vw} \qquad (5\text{-}7)$$

where C_s is the concentration of mercury in the soil in µg/kg and B_{vw} is the soil-to-plant bioconcentration factor (at equilibrium) determined on a wet weight basis (i.e., fresh plant):

$$B_{vw} = \frac{\text{concentration of mercury in plant (µg/kg wet plant)}}{\text{concentration of mercury in soil (µg/kg wet plant)}} \qquad (5\text{-}8)$$

Travis and Arms (1988) proposed the following correlation for B_{vw}, which is valid for mercury:

$$B_{vw} = 38.73\ K_{ow}^{-0.578} \qquad (5\text{-}9)$$

where K_{ow} is the octanol-water partition coefficient. Thus, for H^0g, the value of $B_{vw} = 0.014$ using a $\log K_{ow} = 5.95$ (see Section 5.2.2).

Air-to-Leaf Bioconcentration Factor

Vapor-phase bioconcentration factor for various airborne contaminants from the atmosphere to vegetation can be expressed following the approach of Bacci et al. (1990). These authors suggested that the air-to-leaf route should be regarded as the main mode of contamination for higher plant leaves, mosses and lichens for non-polar, volatile chemicals. The dimensionless air-to-leaf bioconcentration factor can be expressed as

$$B_{vaw} = \frac{C_{va}\rho_p}{C_a F_v} \qquad (5\text{-}10)$$

where C_{va} is the chemical concentration in the plant on a fresh plant mass basis (e.g., μg/kg), C_a is the concentration of a chemical in the air (e.g., μg/m^3), and F_v represents the fraction of the chemical in the vapor phase, and ρ_p is the fresh (i.e., wet) plant density (e.g., kg/m^3). If mercury is assumed to exist in air entirely as a vapor, then F_v equals 1. B_{vaw} represents the air-to-leaf bioconcentration factor on a wet plant mass basis. It has been suggested that B_{vaw} can be correlated with the chemical's water-air and octanol-water partition coefficient and the leaf properties (Bacci et al., 1990).

No measured or estimated values of bioconcentration factors for mercury were found for root uptake air-to-leaf, and deposition routes for mercury. Although B_{vaw} has not been measured for mercury, air-to-leaf correlations (which are appropriate to use for mercury) have been proposed in the literature

$$B_{vaw} = 5.0 \times 10^{-6} K_{ow}/H \qquad \text{(Travis and Blaylock, 1992)} \qquad (5\text{-}11)$$

where B_{vaw} is the air-to-leaf bioconcentration factor (on a fresh plant basis), K_{ow} is the octanol/water partition coefficient as previously defined, and H is the Henry's Law constant in atm·m^3/mol.

Using, for example, a K_{ow} value of 8.9×10^5 and H value of 9.1×10^{-3} atm·m^3/mol for Hg^0, a value of 490 was obtained for B_{vaw} from Eq. 5-11. This value indicates that, for the portion of mercury present in the vapor phase, air-to-leaf transfer can be a major pathway for bioconcentration in vegetation.

5.2.4.2 Biotransfer Factors

The biotransfer factor (B_{TF}) concept addresses chemical accumulation in the receptor through food uptake. It has been suggested in the literature that the biotransfer factor (B_{TF}) may be more useful than BCFs in addressing exposure via food uptake since chemical exposure to feedstock animals may occur through both food and water pathways (Travis and Arms, 1988).

At steady state, the pathway specific biotransfer factor, B_{TFi}, for pathway i, can be expressed as

$$B_{TFi} = C_j/L_iC_{in} \tag{5-12}$$

and the overall biotransfer factor can be expressed as (Cohen, 1989)

$$B_{TF} = C_j \Big/ \left(\sum_{i=1}^{N} L_i \; C_{in} \right) = \left[\sum_{k=1}^{N} (Ex_k H_{kj}) + K_j V_j \right]^{-1} \tag{5-13}$$

V_j is the volume of the receptor and C_j and C_{in} are the concentrations of the contaminant in the receptor (or target organ) and the media associated with the receptor route. L_i represents the intake rate and Ex_k is the outflow stream associated with the particular pathway. H_{kj} is the partition coefficient between receptor j and outflow (or elimination) stream k. The overall biochemical transformation of a given contaminant via first order reaction kinetics is given by the rate constant K_j. For example, one can define a B_{TF} for the concentration of a contaminant in cow's milk where ΣL_iC_{in} is the total contaminant intake during grazing, water drinking, and inhalation. In general, the B_{TF} is not constant since V_j, the volume of the receptor, may vary with time, and the partition coefficient, H_{kj}, and the reaction rate constant, K_j, are likely to be a function of the activity of the receptor. Thus, one is led to conclude that B_{TF} and B_{TFi} are likely to be time variant parameters. Despite this concern, the concept of biotransfer factors and their correlations with K_{ow} are rooted in environmental exposure assessment. BTF values for mercury have not been found in the lieterature and available BTF-K_{ow} correlations (e.g., Travis and Arms, 1988) may not be applicable for mercury although they can be used for order of magnitude analysis.

5.3 Intermedia Transport Parameters of Mercury

The following subsections define the specific intermedia transport factors considered in this study and the reported and estimated parameter values.

5.3.1 Diffusion Coefficients in Air and Water

Molecular diffusion is the net transport of a molecule within a single phase (e.g., liquid or gas) that results from intermolecular collisions rather than turbulence or bulk transport. Diffusion can result from pressure, temperature, and concentration gradients but under environmental conditions, only diffusion due to concentration gradient is considered. The diffusive flux due to concentration gradients is defined by Fick's Law as:

$$J_A = -D_{AB}\, dC_A/dx \tag{5-14}$$

in which J_A is the diffusion flux for compound A (e.g., mg/m²s), dC_A/dx is the concentration gradient along the x direction and D_{AB} is the diffusion coefficient of A in medium B (e.g., units of cm²/s). For example, for air/water exchange processes, molecular diffusion dominates chemical transport near the air/water interphase (in both the air and water phases). In general, the mass flux, N (e.g., mg/m²·s), across an interface (between two phases) is expressed by an equation of the form

$$N = K\Delta C \tag{5-15}$$

in which ΔC is an appropriate concentration driving force and K is a corresponding transfer coefficient. Correlations of mass transfer coefficients include a dependence on the molecular diffusivity, which can be estimated as described below.

Lindberg et al. (1992) reported an Hg^0 diffusion coefficient in air of 0.70 cm²/s. Fitzgerald (1989) reported an Hg^0 diffusion coefficient in water of 2.9×10^{-5} cm²/s. Travis and Blaylock (1993) reported an Hg^0 diffusion coefficient in water of 4.32×10^{-5} cm²/s and an Hg^0 diffusion coefficient in air of 0.66 cm²/s. Diffusion coefficients in air can be estimated by using the Fuller et al. (1966) correlation

$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P\,(V_A^{1/3} + V_B^{1/3})^2} \text{ , cm}^2/\text{s} \text{ , where } M_r = \frac{M_A + M_B}{M_A\, M_B} \qquad (5\text{-}16)$$

in which the subscripts B and A denote the solute and solvent, respectively, T is the temperature (K), M is the molecular weight, P is the pressure (atm), and V_A and V_B are the molar volumes (cm^3/mol) for air and the gas in question, respectively.

Diffusion coefficients in air can also be estimated using the Wilke and Lee (1955) method as given below.

$$D_{BA} = \frac{B' T^{3/2} \sqrt{M_r}}{P \sigma_{AB}^2\, \Omega} \text{ , } \quad \text{cm}^2/\text{s} \qquad (5\text{-}17)$$

where

$$B' = 0.00217 - 0.00050 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

$$M_r = (M_A + M_B)/M_A M_B$$

σ_{AB} = characteristic length of molecule A interacting with B, Å (Reid et al., 1987)

M = molecular weight

T = temperature (K)

P = pressure (atm)

Ω = collision integral (see Lyman et al., 1990; Reid et al., 1987)

Correlations commonly used to estimate diffusion coefficients in water are given below.

Wilke and Chang (1955)

$$D_{BW} = \frac{7.4 \times 10^{-8} (\varnothing_W M_W)^{1/2} T}{\eta_W V_B^{0.6}} \quad , \quad cm^2/s \tag{5-18}$$

where M_W is molecular weight of water (g/mol), T is temperature (K), η_W is viscosity of water (cP), V_B is molar volume of solute B at its normal boiling temperature (cm^3/mol), and $\varnothing_W$ is the solvent association factor which equals 2.6 for water (Wilke and Chang, 1955).

Hayduk and Laudie (1974)

$$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14} V_B^{0.589}} \quad , \quad cm^2/s \tag{5-19}$$

where η_w is viscosity of water (cP), V_B is molar volume (cm^3/mol).

Hayduk et al. (1982)

$$D_{BW} = 1.25 \times 10^{-8} \left(V_B^{-0.19} - 0.292\right) T^{1.52} \eta_W^{\epsilon^*} \quad , \quad cm^2/s \tag{5-20}$$

where V_B is molar volume (cm^3/mol), η_W is viscosity of water (cP), and $\epsilon^* = (9.59/V_B)-1.12$.

5.3.2 Gaseous Mass Transfer Across the Air-Water Interface

The traditional approach to calculating the flux of a compound between air and water phases is to use the two-film theory in which it is assumed that the concentrations immediately on either side of the interface are in equilibrium as can be expressed by a Henry's Law constant (Lewis and Whitman, 1924). The flux, N, can be expressed as:

$$N = K_G (C_g - H'C_l) = K_L (C_l - C_g/H') \tag{5-21}$$

where K_G and K_L are the overall mass transfer coefficients (cm/s) for the gas and liquid phase, respectively, H' is a unitless Henry Law's constant, and C_g and C_l are concentrations in gas and liquid phase, respectively. The overall mass transfer coefficients for the gas and liquid phase can be defined as:

$$1/K_G = 1/k_g + H'/k_l \tag{5-22}$$

$$1/K_L = 1/k_l + 1/H'k_g \tag{5-23}$$

where k_g is a gas-phase mass transfer exchange coefficient (cm/s) and k_l is a liquid-phase mass transfer coefficient. The important parameters that are needed in order to predict N are H' and the mass transfer coefficients k_g and k_l. The mass transfer coefficients depend on the prevailing turbulence level (as determined by water currents or wind), on temperature, on properties of the solute such as diffusivity, or molecular size (Mackay and Yeun, 1983), and on the depth of the water body (Cohen, 1986). Thus, one must ensure that k_g and k_l are determined for the appropriate environmental conditions. Predictive equations, appropriate for screening-level analysis, that can be used to estimate k_g and k_l are given in Sections 5.3.2.1 and 5.3.2.2.

5.3.2.1 Air/Water - Air Side - Mass Transfer Coefficient (k_g) for Mercury

Numerous theories and empirical equations have been proposed to predict k_g. The theoretical expressions for k_g as proposed by Brutsaert (1975) are particularly useful for predicting k_g. For a rough surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^{+}\left(C_D^{-1/2} - 5\right) + 7.3\ Re_o^{0.25}\ Sc_a^{1/2}\right]^{-1}, \quad Re_o > 2 \tag{5-24}$$

and for a smooth surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^{+}\left(C_D^{-1/2} - 13.5\right) + 13.6\ Sc_a^{2/3}\right]^{-1}, \quad Re_o < 0.13 \tag{5-25}$$

in which the Schmidt number, Sc_a, is given by the ratio ν_a/D_a, where D_a is molecular diffusivity in air (Section 5.3.1), U_{10} is the wind speed at a reference height (usually 10 meters), C_D is the wind drag (or stress) coefficient, ϵ_D^+ is the ratio of the eddy momentum diffusivity (ϵ_m) to the eddy mass diffusivity (ϵ_D), often approximated to be near unity, and Re_o is the roughness Reynolds number. Eqs. 5-24 and 5-25 are strictly applicable to a neutral atmospheric condition. However, as suggested by Brutsaert (1975), Eqs. 5-24 and 5-25 are probably still satisfactory even under very unstable, but apparently not under stable conditions. For non-neutral conditions, the mass flux equations Eq. 5-21 must be used with caution since the bulk gas phase concentration as used in Eq. 5-21 may lie outside the dynamic sublayer (Brutsaert, 1975). Under such conditions, a detailed air quality model which considers the concentration profile at the air-side must be considered. Thus, one should regard the use of the estimation methods for k_g as given in this section as suitable for neutral conditions and for screening-level analysis for non-neutral conditions. The prediction of k_g for non-neutral conditions can be accomplished using the approach as presented by Brutsaert (1975). However, it should be noted that within the context of screening-level analysis, as is the case in the CAPCOA model, the application of Eqs. 5-24 and 5-25 is sufficient especially for sparingly soluble hydrophobic organic compounds.

The use of Eqs. 5-24 and 5-25 requires the wind drag coefficient velocity as input. The wind-drag coefficient, C_D, is defined as (Wu, 1980)

$$C_D = \left(\frac{U_W^*}{U_{10}}\right)^2 \left(\frac{\rho_w}{\rho_a}\right) = \left(\frac{U_a^*}{U_{10}}\right)^2 \tag{5-26}$$

in which U_W^* is the surface shear velocity given by:

$$U_W^* = \sqrt{\frac{\tau_s}{\rho_w}} \tag{5-27}$$

where τ_s is the shear stress imparted by the wind on the water surface, ρ_w is the water density, ρ_a is the air density, and U_{10} is the wind speed measured at a reference height (usually 10m) above the water surface. It is noted that the water-side friction velocity U_w^* and U_a^* are related through the simple relation $\rho_a(U_a^*)^2 = \rho_w(U_w^*)^2$ which arises from the condition of stress equality at the air/water interface. Given wind speed profile data, one can estimate U^*_a using the following equation:

$$U_a^* = U_{10}\, k \left[\ln\left(\frac{z_{10}}{z_o}\right) - \psi_M\left(\frac{z}{L}\right) + \psi_M\left(\frac{z_o}{L}\right) \right]^{-1} \tag{5-28}$$

where k is the von Karman constant (k = 0.4), U_{10} is the velocity at the reference height, z_{10}, ψ_M is a stability function, and L is the Obukhov stability parameter (Holtslag and Van Ulden, 1983; and reference therein). It is noted that for neutral conditions the function ψ_M is set to zero. The roughness Reynolds number, Re_o, is defined by:

$$Re_o = U_a^*\, z_o/\nu_a \tag{5-29}$$

where z_o is the effective surface roughness height and ν_a is the kinematic viscosity of air. The effective surface roughness height can be estimated for smooth water surfaces as (Brutsaert, 1975)

$$z_o \approx 0.135(\nu_a/U^*_a) \ , \qquad \text{cm} \tag{5-30}$$

and for a rough surface,

$$z_o = a(U^*_a)^b \quad , \qquad \text{cm} \tag{5-31}$$

in which U^*_a is the air-side friction velocity (cm/s) and ν_a is the kinematic viscosity (cm/s^2). The parameters a and b are given by $a = 1.69\times10^{-2}$ and $b = -1$ for $U^*_a \le 6.89$ cm/s, and $a = 1.65\times10^{-4}$, $b = 1.4$ for $U^*_a > 6.89$ cm/s (Jirka and Brutsaert, 1984). An alternative correlation for z_o was proposed by Wu (1980) for a large water fetch in which z_o was expressed by:

$$z_o = 0.0144(U^*_a)^2/g \quad , \qquad (g=981,\ \text{cm/s}^2) \tag{5-32}$$

For a large water fetch, the wind-stress coefficient near neutral conditions can be estimated from (Cohen, 1983)

$$C_D = 8.5\times10^{-4} \quad , \qquad U_{10} < 5\ \mathrm{m/s} \tag{5-33}$$

$$C_D = [0.85 + 0.11\,(U_{10} - 5)]\times10^{-3} \quad , \qquad 5\ \mathrm{m/s} \le U_{10} \le 20\ \mathrm{m/s} \tag{5-34}$$

$$C_D = 2.5\times10^{-3} \quad , \qquad U_{10} > 20\ \mathrm{m/s} \tag{5-35}$$

or (Wu, 1980)

$$C_D = (0.8 + 0.065U_{10})\times10^{-3} \quad , \qquad U_{10} \ge 1\ \mathrm{m/s} \tag{5-36}$$

Other alternate expressions for k_g under neutral (or near-neutral) conditions have been proposed in the literature. For example, Lyman et al. (1990) recommends the correlation of Southworth (1979) for k_g

$$k_g = 1137.5\,(V_{wind}+V_{curr})\sqrt{\frac{18}{MW}} \quad , \qquad \mathrm{cm/hr} \tag{5-37}$$

where V_{wind} and V_{curr} are the velocities of the wind and water current, respectively (m/s), and MW is the molecular weight of the contaminant of interest. As an example, using V_{wind} = 3 m/s and V_{curr} = 1 m/s, k_g for mercury is estimated as 1362 cm/hr. It is important to note that the atmospheric stability condition for which Eq. 5-37 applies was not reported. Moreover, the theoretical basis of the Southworth (1979) equation is questionable because of the linear additivity of the wind and air currents in Eq. 5-37. The hydrodynamic effects of the wind relative to the water current on the roughness and velocity of the water surface are likely to be very different, as supported by later researchers (cited by Cohen, 1986) who have found that the effect of wind velocity and current velocity on k_g vary by different powers. Finally, a convenient correlation for k_g, determined based on laboratory measurements in a small wind-wave tank (fetch < 3m) under near neutral conditions, was proposed by Mackay and Yeun (1983).

$$\frac{k_g}{U_a^*} = 46.2 \times 10^{-3}\ Sc_a^{-0.67} \tag{5-38}$$

Eq. 5-38 results in k_g values which are about 20%-40% higher than predicted by Eqs. 5-24 and 5-25. The higher prediction by the Mackay and Yeun (1983) correlation may be, in part, due to the difference in surface roughness condition in their short fetch wind-wave tank, for a given U_a^*, relative to the condition that would exist at long fetch.

5.3.2.2 Air/Water - Liquid Side - Mass Transfer Coefficient (k_l) for Mercury

The water-side mass transfer coefficient, k_l, for large water bodies (i.e., reservoirs, lakes, oceans) can be estimated using the theoretical correlation of Cohen and Ryan (1985), which was found to be in excellent agreement with available data for a water-side friction velocity in the range of 0.5-6 cm/s,

$$k_l/U_w^* = a\ Sc_w^{-n} \tag{5-39}$$

in which Sc_w is the Schmidt number given by the ratio ν_w/D_w where ν_w is the water kinematic viscosity and D_w is the chemical molecular mass diffusivity in water. The constants a and n are weak functions of the dimensionless water surface velocity U_s^+ ($U_s^+ = U_s/U_w^*$, in which U_s is the wind-induced surface water velocity), given by:

$$\begin{aligned} a &= a_0 - a_1 \ln U_s^+ \\ n &= n_0 - n_1 \ln U_s^+ \end{aligned} \tag{5-40}$$

where

$$\begin{aligned} a_0 &= 0.09691;\ a_1 = 0.01053; \\ n_0 &= 0.5778;\ n_1 = 0.01771 \end{aligned} \tag{5-41}$$

For a long fetch (say ≥ 30m), the surface velocity is equal to about 3.5% of the wind speed (i.e., $U_s = 0.035\ U_{10}$), while for short fetch (say less than about 10m), $U_s \approx 0.020\ U_{10}$

(Wu, 1975; Plate and Friedrich, 1984). Eq. 5-39 was found to be in excellent agreement with laboratory data from wind-wave facilities with an average error of about 16 percent.

The prediction of k_l in flowing water bodies (e.g., rivers) requires consideration of the river current and the river depth (Cohen, 1986). There are numerous studies on the reaeration coefficient in flowing streams (O'Connor, 1983), and the water-side mass transfer coefficient k_l can be estimated from the reaeration coefficient, k_v (e.g., hr^{-1}), by using the following relation:

$$k_l = \left(\frac{D}{D_o}\right)^{1/2} h\, k_v \tag{5-42}$$

in which h is the depth of the water body (e.g., m), D is the mass diffusivity of the compound of interest (e.g., mercury) D_o is the mass diffusivity of oxygen in water at 20°C, and h is the river depth (Cohen, 1986). Lyman et al. (1982) recommended the following empirical correlations, which are based on field data, for predicting k_v:

$$k_v = 1.08\,(1 + 0.17\,F^2)\,(V_{curr}\,S)^{0.375},\ \ hr^{-1} \tag{5-43}$$

$$k_v = 0.00102\,V_{curr}^{2.695}\,h^{-3.085}\,S^{-0.823},\ \ hr^{-1} \tag{5-44}$$

$$k_v = 638\,V_{curr}\,S,\ hr^{-1} \tag{5-45}$$

in which S is the river bed slope (m drop/ m run), F is the Froude number ($F = V_{curr}/gh$), and h is the river depth (m). The use of an average value of k_v determined from the above three equations was recommended by Lyman et al. (1982). Other relations for k_v that are suitable when bed slope information is not available were recommended by Lyman et al. (1990), Shen (1992), and Shen et al. (1993). For example, the empirical correlation which was recommended by Shen (1992) and Shen et al. (1993) can be written as

$$k_v = 22.05\,(1.024)^{T-20}\,U_s^{0.67}\,h^{-1.85} \qquad , \qquad hr^{-1} \tag{5-46}$$

in which T is the temperature (°C), U_s is the water current (m/s), and h is the water depth (m).

Example:

In order to estimate K_L for a neutral atmospheric condition, proceed along the following steps:

1) Select temperature, wind speed, and the correlation appropriate for the water body of interest.
2) Select a value of the dimensionless Henry's Law constant for the selected mercury compound from Table 5-7.
3) Determine the value of k_l from a suitable correlation selected from Section 5.3.2. once a wind speed and type of water body are selected.
4) Determine k_g from either Eq. 5-24 or 5-25 depending on the resulting value for Re_0 with linear interpolation of k_g in the region $0.13 \leq Re_0 \leq 2$. Note that a value for U^*_a is required and this can be estimated from Eqs. 5-26, 5-33 - 5-35, and 5-36 or from wind speed profile data.
5) Use Eq. 5-23 to determine K_L.

6.0 FATE AND TRANSPORT OF MERCURY IN ENVIRONMENTAL MEDIA

The chemistry of mercury which is of environmental significance is that of elemental mercury contributed from natural degassing (volatilization of biogenic mercury from the lithosphere and hydrosphere) and anthropogenic emissions. The distribution of elemental mercury in the environment is affected by the following major processes (USDHHS, 1992):

- Oxidation and complexation
- Wet and dry deposition
- Soil and sediment sorption
- Bioaccumulation

Mercury deposited to water or soil from the atmosphere may dissolve and become bound to dissolved organic carbon (DOC) and become mobile. Some of the mercury bound to DOC may be sorbed, some will be reduced by both biotic and abiotic processes, and some of the mercury in soils may be leached into groundwater and runoff water (Schroeder, 1989). The distribution of mercury among these environmental media is related to pH, oxygen content, organic matter, and reducing agents (Iverfeldt and Lindqvist, 1984), as well as biota such as microbes and earthworms (Bodek et al., 1988; Andersson et al., 1990). Determining the fate of mercury is complicated by the formation of inorganic and organic compounds which may be soluble or insoluble (Schroeder, 1989). Organic compounds can be bioaccumulated or volatilized while inorganic compounds may precipitate to sediment. These transformation and distribution processes are briefly discussed with respect to environmental media (air, water, soil, and biota) in the following subsections.

6.1 Mercury in Air

Annual global emissions are on the order of 10^6 kg/yr (Nriagu, 1979; Schroeder et al., 1991; USDHHS, 1992), the majority of which are from degassing of elemental mercury from the lithosphere and hydrosphere. In addition, volatilization from vascular plants, plankton, algae, and soil provide a significant flux of mercury into the air. Anthropogenic emissions account for only 10-30% of total annual emissions (Nriagu, 1979; USDHHS, 1992).

Reported atmospheric lifetimes for mercury range from 90 days to 2 years depending on the partitioning between various forms of mercury and the meteorological conditions (WHO, 1976; Nriagu, 1979; USEPA, 1984; WHO, 1990; USDHHS, 1992). Soluble mercury species may have atmospheric lifetimes on the order of several weeks (WHO, 1990). Lifetimes of this length can result in transport of mercury throughout the globe. Typical ambient concentrations of mercury in various locations are presented in Table 6-1.

Table 6-1. Concentration of Hg Vapor and Particulate Hg in Various Atmospheres

Study Area	Hg Concentration (ng/m^3) Vapor	Particle
Remote marine	1-3	0.0004-0.002
Rural	3-10	
Urban	2-30	0.2-0.3
Large cities	5-50	
Industrial	10-50	
Chloroalkali waste ponds	60-1000	0.02-04
Cinnabar deposits	30-1600	
Power plant plume	200-1700	2-150
Volcanic and geothermal vents	10-40,000	

Source: Lindberg, 1987

6.1.1 Atmospheric Chemistry

Atmospheric mercury consists primarily of four chemical forms: elemental mercury (Hg^0), mercuric chloride ($HgCl_2$), monomethylmercury chloride (CH_3HgCl), and dimethylmercury ($(CH_3)_2Hg$) (Iverfeldt and Lindqvist, 1984; Schroeder et al., 1991). Table 6-2 shows the approximate distribution of these species in the atmosphere.

Mercury's substantial vapor pressure is consistent with the estimate that 95%-99% of total airborne mercury occurring in the vapor phase (Iverfeldt and Lindqvist, 1984; WHO, 1990; Schroeder et al., 1991; USDHHS, 1992). An exception to this pattern occurs in the immediate vicinity of industrial sources, such as coal-fired plants, where the particle phase concentrations may surpass gaseous phase concentrations. However, the mercury is converted to the gaseous phase within several km of the source (Lindberg, 1987). In addition, according to Nriagu (1979) and Lindberg (1987), greater than 90% of dry deposition occurs at distances greater than 20 km from the source. Therefore, it is expected that only minimal amounts of particle-bound mercury will be available for transfer to other phases or for exposure via inhalation. Based on these observations, this report considers atmospheric mercury to be primarily in the gaseous phase.

6.1.1.1 Gaseous Phase Reactions

The most important atmospheric transformation for mercury is the oxidation of mercury emitted in the elemental form to divalent mercury (Hg^{++}). This conversion allows for subsequent complexation of mercury to inorganic salts which have increased water solubilities. Increases in the level of atmospheric oxidants will facilitate the above process (Iverfeldt and Lindqvist, 1986; Lindberg et al., 1987). The polluted troposphere contains numerous potential oxidants including O_2, O_3, NO_2 as well as the radicals H_2O_2, NO_3, HO_2, OH, and RO_2. The gaseous phase reaction of mercury with O_3 is considered the most important atmospheric oxidation pathway (Iverfeldt and Lindqvist, 1986).

Table 6-2. Speciation of Mercury in the Atmosphere

Species	Percent of Total Atmospheric Mercury
Elemental mercury	50
Inorganic mercury	25
Monomethylmercury	21
Dimethylmercury	1
Particle-bound mercury	3

Source: Nriagu, 1979; Harrison, 1986

Atmospheric Hg^0 is oxidized by O_3 to Hg^{++} via gas phase reaction. The first order rate constant for this reaction is 1.7×10^{-18} cm^3/molec·sec at 20°C (Schroeder et al., 1991). Oxidized mercury (Hg^{++}) can complex with anions present in the atmosphere, primarily chlorine, to form compounds with the HgX_2 structure. Menke and Wallis (1980) reported that elemental Hg can also react directly with molecular chlorine to form $HgCl_2$. The first order rate constant for this reaction (assuming $[Cl_{2(g)}] = 4.4$ mg/m^3) equals 4×10^{-16} cm^3/molec·s at 20°C. Menke and Wallis (1980) also reported the reaction of Hg^0 with H_2O_2 to form $Hg(OH)_2$, with a reaction rate of 4×10^{-16} cm^3/molec s at 20°C. Niki et al. (1983) (reported by Atkinson, 1989) measured the reaction of OH radicals with dimethylmercury which proceeds via a displacement process

$$OH + CH_3HgCH_3 \rightarrow CH_3HgOH + CH_3 \qquad (6\text{-}1)$$

followed by subsequent oxidation of the CH_3 radical to formaldehyde and other minor products, and by further homogeneous and/or heterogeneous reactions of CH_3HgOH to yield compounds such as $[(CH_3Hg)_3O]NO_3$. The measured reaction rate constant for this reaction is $19.7 \pm 1.6 \times 10^{-12}$ cm^3/molec·s. Assuming an atmospheric OH concentration of 5×10^5 molec/cm^3, this reaction rate corresponds to an atmospheric lifetime of 28 hours.

Atmospheric oxidation and complexation of mercury can also occur via aqueous phase reactions in clouds and fog. Aqueous phase oxidation rates are generally several order of magnitude higher than rates of gaseous phase reactions (Iverfeldt and Lindqvist, 1984). These reactions are described in Section 6.1.1.2. The main gaseous and aqueous phase reactions of mercury in the atmosphere are presented in Table 6-3.

Many atmospheric compounds are subject to transformations caused by direct photolysis. Schroeder et al. (1991) measured the absorption cross section (σ) of elemental mercury and found no absorption at wavelengths greater than 253.6 nm. Since the troposphere only experiences electromagnetic radiation at wavelengths greater than 290 nm, mercury will not undergo any direct photochemical oxidation. However, dimethylmercury which is volatilized from water or soil can be photolyzed in the atmosphere to elemental

Table 6-3. Atmospheric Chemical Kinetic Mechanism of Mercury

Reaction		Equilibrium or Reaction Rate Parameter
1.	$Hg^0(g) + O_3(g) \rightarrow Hg(II)$	1.7×10^{-18} cm^3 molec^{-1} s^{-1}
2.	$Hg^0(g) + Cl_2(g) \rightarrow HgCl_2(g)$	4.1×10^{-16} cm^3 molec^{-1} s^{-1}
3.	$Hg^0(g) + HCl(g) \rightarrow$ products	1.5×10^{-17} cm^3 molec^{-1} s^{-1}
4.	$2Hg^0(g) + O_2(g) \rightarrow 2HgO(s,g)$	1×10^{-23} cm^3 molec^{-1} s^{-1}
5.	$Hg^0(g) + H_2O_2(g) \rightarrow Hg(OH)_2(g)$	4.1×10^{-16} cm^3 molec^{-1} s^{-1}
6.	$Hg_2^{2+}(aq) \rightleftharpoons Hg^0(aq) + Hg^{2+}$	$K = 2.9\times10^{-9}$ M
7.	$Hg^{2+}(aq) + SO_3^{2-}(aq) \rightleftharpoons Hg(SO)_3(aq)$	$K = 5.0\times10^{-12}$ M^{-1}
8.	$HgSO_3(aq) + SO_3^{2-}(aq) \rightleftharpoons Hg(SO_3)_2^{2-}$	$K = 2.5\times10^{11}$ M^{-1}
9.	$Hg^0(aq) + O_3 \rightarrow Hg(II) + O_2$	4.7×10^{7} M^{-1} s^{-1}
10.	$Hg(SO_3)_2^{2-}$ (aq) $\rightarrow Hg^0$	1×10^{-4} s^{-1}
11.	$HgSO_3$ (aq) $\rightarrow Hg^0 + SO_3^{2-}$	0.6 s^{-1}
12.	$Hg^{2+} + 2OH \rightleftharpoons Hg(OH)_2$	NA
13.	$Hg^{2+} + 2Cl \rightleftharpoons HgCl_2$	NA
14.	$(CH_3)_2Hg + OH \rightarrow CH_3HgOH + CH_3$	19.7×10^{-12} cm^3 molec^{-1} s^{-1} (1)

Source: Wrobel et al., 1993

NA = Not Available

(1) from Atkinson, 1989

mercury and two methyl radicals (Bodek et al., 1988). Figures 6.1 and 6.2 show an overview of the atmosphere chemistry of inorganic and dimethylmercury, respectively.

6.1.1.2 Aqueous Phase Reactions

In addition to the gaseous phase, atmospheric mercury can exist in the aqueous phase. Aqueous phase reactions occur in clouds, fog, rain-water, or snow. Measured concentrations of mercury in precipitation are presented in Table 6-4. These concentrations exceed those predicted by Henry's Law ($6\text{-}16 \times 10^{-3}$ ng/L) by three orders of magnitude. This suggests that the atmosphere contains appreciable amounts of gaseous (or particle-bound) mercury which are more soluble in water than elemental mercury. These compounds result from the oxidation and complexation of elemental mercury to inorganic ligands, forming species with higher solubility than Hg^0. Iverfeldt and Lindqvist (1986) measured oxidation of aqueous Hg^0 and found the following two aqueous phase reactions occur:

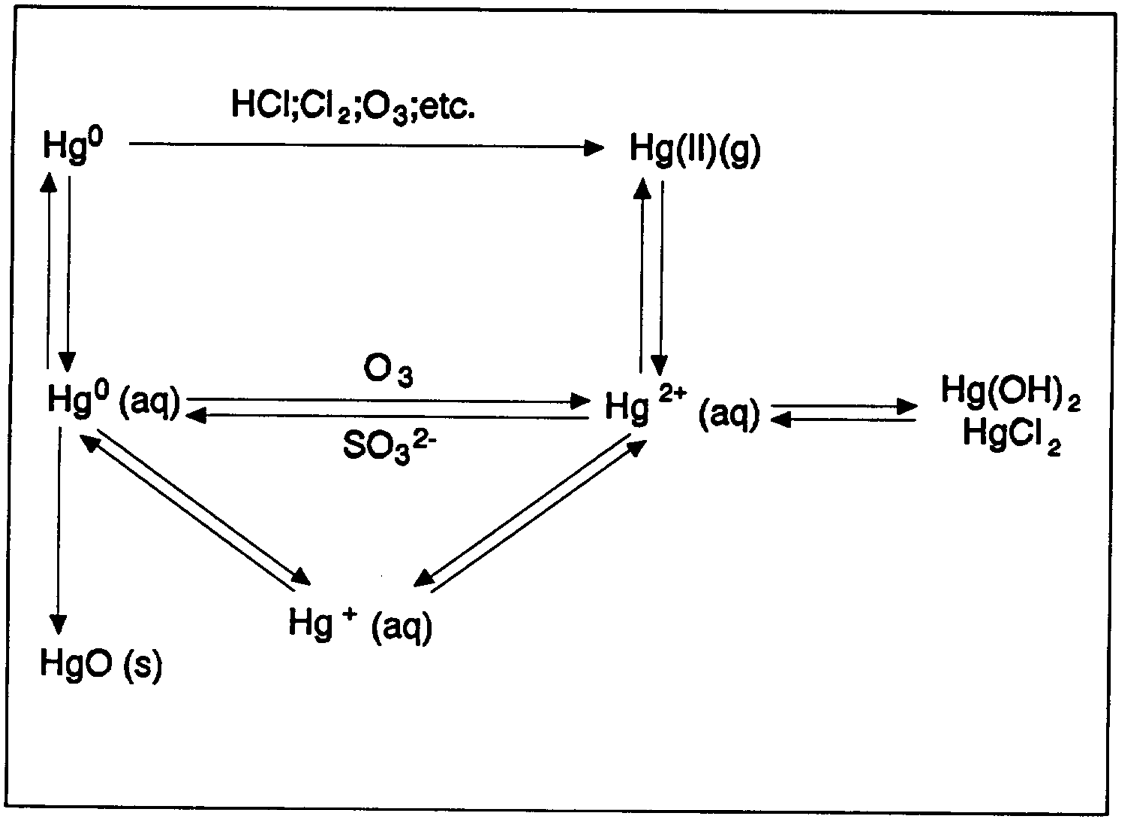
$$O_3 + H_2O + Hg^0 \rightarrow O_2 + 2OH^- + Hg^{++} \tag{6-2}$$

$$H_2O_2 + 2H^+ + Hg^0 \rightarrow 2H_2O + Hg^{++} \tag{6-3}$$

Following either of these reactions divalent Hg will complex with whatever anions are present in the atmosphere, resulting is inorganic mercury complexes with increased solubility. In general the oxidation potential of the atmosphere will increase with decreasing pH (Schroeder et al., 1991). Whether the conversion of elemental mercury to higher solubility complexes occurs primarily in the gaseous phase or after dissolution in cloud-water is unclear.

6.1.2 Dry Deposition

Dry deposition may be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation (Davidson and Wu, 1989). Dry deposition is affected by a multiplicity of factors that often interact in complex ways. The most important factors are the characteristics of the atmosphere (e.g.,



Hg^0
$HCl;Cl_2;O_3$;etc.
Hg(II)(g)
Hg^0 (aq)
O_3
SO_3^{2-}
Hg^{2+} (aq)
$Hg(OH)_2$
$HgCl_2$
Hg^+ (aq)
HgO (s)

Figure 6.1. **Schematic Description of the Atmospheric Chemistry of Inorganic Mercury**

Source: Wrobel et al., 1993

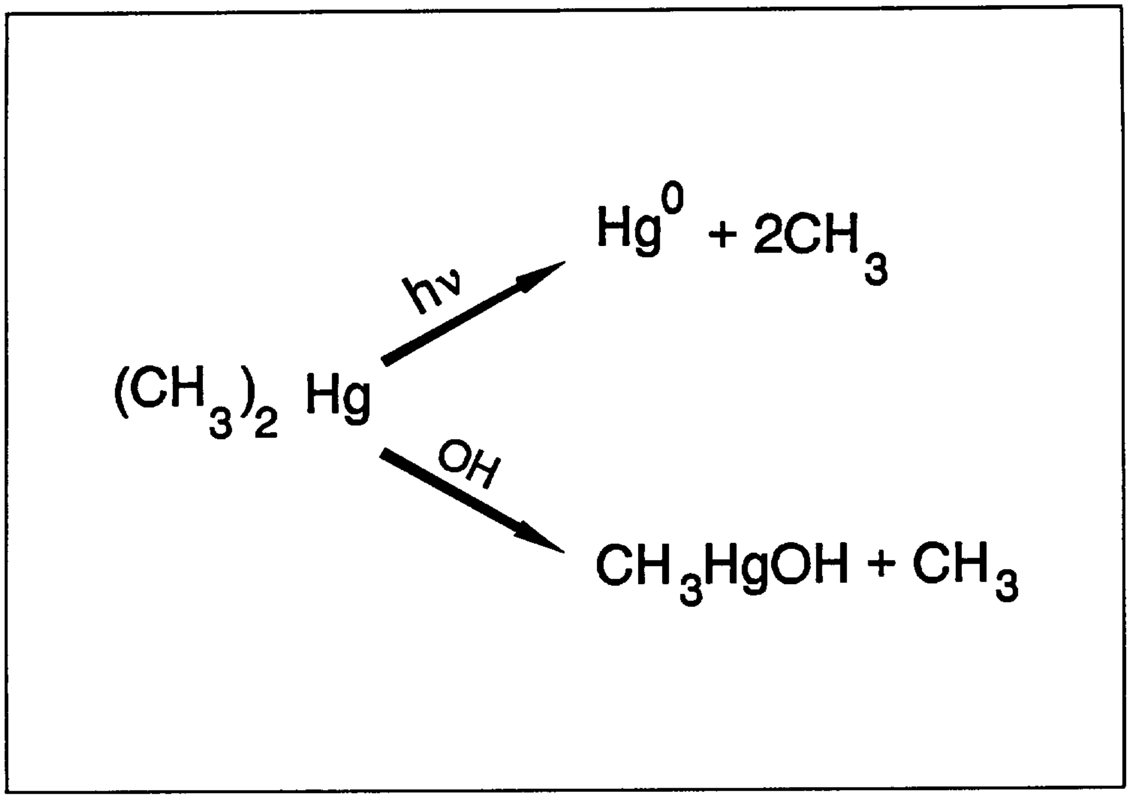

$(CH_3)_2Hg$
$h\nu$
$Hg^0 + 2CH_3$
OH
$CH_3HgOH + CH_3$

Figure 6.2 Schematic Description of the Atmospheric Chemistry of Dimethylmercury

Table 6-4. Summarized Concentrations of Mercury in Precipitation

Type of Area	Rainfall (ng/L)(1) Mean	Rainfall (ng/L)(1) Range	Snowfall (ng/L)(2) Mean	Snowfall (ng/L)(2) Range
Remote Oceanic (3 areas)	6	2-26		
Rural Areas (30 sites)	16	1.3-90	5	
Urban Areas (5 sites)	48	6-122	27	13-40

Notes:

(1) Arranged concentrations from ~18 studies at various locations in the world
(2) Extremely limited data from 4 studies.

Source: Johnson, 1993

wind and stability conditions), the nature of the surface, and properties of the depositing species. Also, solubility and chemical reactivity may be dominant factors affecting capture of gases by surfaces.

The dry deposition flux of a chemical can be expressed by

$$N_A = V_d C_a \tag{6-4}$$

where N_A is the mass flux (e.g., $\mu g/m^2 \cdot s$), C_a is the pollutant concentration in the atmosphere (e.g., $\mu g/m^3$), and V_d is the pollutant dry deposition velocity (e.g., m/s).

Dry deposition velocities can vary by several orders of magnitude depending on the surface characteristics (e.g., type of vegetative cover), the chemical type, and meteorological conditions. Dry deposition is expected to be an important atmospheric removal mechanism for mercury. Xiao et al. (1991) found that temporal variations in deposition velocity of elemental mercury correlated with daily and seasonal temperature cycles. The deposition flux of particle bound mercury is generally lower, or in the same range as that of gaseous Hg^0. Lindberg et al. (1992) found the dry deposition velocity of particle-bound elemental mercury to range from 0.02 cm/s to 0.11 cm/s. However, particle-bound mercury comprises less than 5% of total airborne mercury and exists primarily in the fine fraction (Lindberg et al., 1991). Therefore, dry deposition of particle-bound atmospheric mercury is of less significance compared to dry deposition of gaseous mercury (Lindberg et al., 1992).

In general, Xiao et al. (1991) found that the deposition velocity for mercury onto tree canopies is lowest in the winter due to loss of leaves and lower temperatures. Deposition to leaves is controlled by opening of the stomata and uptake by the mesophyll (middle layer of leaves). Deposition rate is largely governed by the resistance to uptake of insoluble Hg^0 by the mesophyll, which is approximately 70% water (Curtis, 1983). Some Hg^0 may be oxidized, via aqueous phase reactions, in leaf surface water films to more soluble Hg^{++}, thus increasing the deposition velocity (V_d) (Lindberg et al., 1991). Soluble forms of mercury will exhibit more efficient removal by dry deposition due to lower resistance at the leaf mesophyll and dissolution into water films on the surface of leaves.

Table 6-5 summarizes the measured dry deposition velocities of Hg^0 reported in the literature, which range from 0.006 to 0.12 cm/s depending on the season and the surface onto which deposition takes place.

6.1.3 Wet Deposition

Wet deposition (scavenging) can increase the overall deposition rate of mercury and thus, increase mercury concentration in the soil, water and vegetation due to direct deposition. Both rain and snow can remove mercury from air; however, snowfall is not considered a significant removal process in most of the heavily populated regions of California. In addition, wet deposition is episodic; therefore, the climatological conditions of the location in question must be considered when evaluating the relative importance of wet deposition as a removal process.

The degree of wet deposition is usually estimated from knowledge of the washout ratio, W, defined as

$$W = C_{rainwater}/C_{air} \tag{6-5}$$

in which $C_{rainwater}$ and C_{air} are the concentrations (e.g., ng/m^3) of mercury in rainwater (at ground level) and in the gaseous phase (i.e., in the atmosphere), respectively. Thus, wet deposition flux (e.g., ng/m^2·hr), $\dot{M}_w$, is given by

$$\dot{M}_w = W \cdot R \cdot C_{air} \tag{6-6}$$

Table 6-5. Dry Deposition Velocity of Mercury

Deposition velocity (cm/s)	Conditions[a]	Reference
0.1	Deciduous forest canopy	Lindberg et al., 1992
0.05-0.075	Coniferous forest	Lindberg et al., 1992
0.06-0.1	Tall grass canopy	Barton et al., 1981
0.006-0.02	Modeled for wintertime conditions	Lindberg et al., 1991
0.10-0.12	Modeled for summertime conditions	Lindberg et al., 1991
0.02-0.11	Aerosols to forest canopy	Lindberg et al., 1991, 1992
0.03-0.1	Alfalfa plants	Lindberg et al., 1979
0.5	NR	Fitzgerald et al., 1991
0.1	NR	Fitzgerald, 1989

NR = Not Reported

[a] all values are measured for dry deposition of gaseous elemental mercury, unless otherwise indicated

where R is the precipitation rate (m/hr). Washout ratios for Hg^0 typically range from 10 to 100 (data from Tables 6-1 and 6-4). Brosset (1987) measured the total concentration of mercury in rainwater and found it to be 10,000 to 50,000 times greater than in ambient air (i.e., washout ratio of 1×10^4 to 5×10^4, indicating that mercury species are concentrated in rain. On average, monomethylmercury comprises 2 to 10% of total mercury in rainwater, while dimethylmercury is typically not found in rainwater (Bloom and Watras, 1989).

Rain scavenging of vapor mercury and mercury compounds can be predicted by adapting the detailed approach described by Tsai et al. (1991) and Clay (1992). However, a simple upper-limit estimate (for non-reactive species) can be obtained by assuming that the raindrops are in equilibrium with the air phase when they reach ground level. This assumption is supported by the analysis of Cohen (1986) and Slinn (1978) which indicates that raindrops falling through 10 meters of polluted atmosphere are nearly at equilibrium with gaseous chemical. Thus, the concentration of the dissolved chemical in rain, $C_w^{(d)}$ (ng/m^3 water), is given by

$$C_w^{(d)} \approx \frac{C_a^{(g)}}{H_{aw}} \qquad (6\text{-}7)$$

in which $C_a^{(g)}$ is the concentration of the chemical in the atmosphere in the vapor phase (e.g., ng/m^3 air), and H_{aw} is the dimensionless Henry's Law constant (i.e., $H_{aw} = C_a^{(g)}/C_w^{(d)}$).

The contribution of wet deposition to total atmospheric deposition of mercury and capture by specific receptors varies based on: (1) the proportional speciation of mercury species; (2) the rate and total rainfall; (3) the ambient temperature; and (4) the surface characteristics (Lindberg et al., 1991). Nevertheless, a survey of published data indicates that on an annual basis, the rate of wet and dry deposition are of comparable magnitude; however, the rate of wet deposition is generally lower than the dry deposition rate, and is responsible primarily for the removal of soluble species of mercury (USDHHS, 1992; Lindberg et al., 1992).

6.1.4 Re-entry of Deposited Mercury to the Atmosphere

Mercury is not only deposited to soil and water, but is also released from these environmental media. These emissions can be due to natural degassing of elemental mercury, or due to volatilization of mercury complexes which have resulted from anthropogenic emissions.

Lindberg et al. (1992), in a field study at the Walker Branch Watershed in Tennessee, found that under all ambient conditions the concentration of Hg^0 generally decreased with increasing height above the ground, indicating that the forest acted as a net source of Hg^0 to the overlying atmosphere. Schroeder et al. (1989) measured mercury in the air over Eagle Lake, Canada, and the land its immediate vicinity. They found a net flux of mercury into the air, with atmospheric mercury concentrations directly over the water being consistently greater than those over the adjacent land. The average day-time flux over foliar landscape varied between 0.6 ± 0.2 to 1.4 ± 0.4 ($\bar{x} = 1.1 \pm 0.4$) ng/m²hr, while those over water ranged between 3.2 ± 0.5 to 20.0 ± 0.9 ($\bar{x} = 6.3 \pm 3.6$) ng/m²hr. Schroeder et al. (1989) also found that following either deposition to leaf surfaces or root uptake, plants re-released mercury to the air via their stomatas. Xiao et al. (1991) found similar concentration gradients over several Swedish lakes and the forest surrounding them, with flux over the lake averaging ten times higher than that over the forest soil. Xiao et al. (1991) also found that the low flux from the forest soil was partially correlated with adsorption of mercury to leaf litter.

The high vapor pressure of elemental mercury (Hg^0) and dimethylmercury ($(CH_3)_2Hg$) makes it likely that they are the species of mercury being emitted from the soil and the water (Schroeder et al., 1989; Xiao et al., 1991). In the three studies cited above, the concentration gradients above the land and water were steeper when the ambient temperature was higher. Furthermore, the slopes of the concentration gradients were correlated with diurnal temperature cycles. The increased emissions at higher temperatures probably resulted from an increase in the rate of microbial reduction of divalent mercury to volatile elemental mercury and an associated increase in vapor pressure of the reduced mercury. In all three studies, the concentration gradients (rate of decrease in concentration with increasing height) decreased during periods of rain, demonstrating that increased deposition due to rainout compensated for re-emission of mercury into the air.

Although dry and wet deposition is the dominant removal mechanism for atmospheric mercury, volatilization of mercury from soil and water usually exceeds deposition. Therefore, the atmosphere should be considered as a mild sink for Hg^0 (Lindberg et al., 1991, 1992; USDHHS, 1992).

6.2 Mercury in Water

The main source of mercury to the water is atmospheric deposition. The majority of mercury deposited to bodies of water from the atmosphere is in the elemental form, although the presence of methylmercury has been reported in rain (Bloom and Watras, 1989; Winfrey and Rudd, 1990; Lee and Iverfeldt, 1991). Sorensen et al. (1990) calculated that, on average, 75% of mercury input to lakes is from direct atmospheric deposition to the surface of the water. The remainder is from watershed inputs, such as surface run-off and groundwater leaching. This latter fraction of mercury enters the lake mostly bound to dissolved organic carbon (DOC). The majority of mercury transported from the surrounding watershed originates from wet and dry deposition to plants and soils.

Flooding of previously dry basins either naturally or intentionally can also lead to high concentrations of mercury in water. When soils which are rich in mercury from either leaching of minerals, accumulation of atmospheric depositions, or industrial activity are flooded, soil bound mercury may solubilize. Additionally, flooding leads to the decomposition and release of stored organics, which stimulate microbial methylation of mercury in newly flooded areas. This methylation is fastest in the surface layer of sediments where microbial activity and newly released organic carbon are concentrated (Winfrey and Rudd, 1990; Andersson et al., 1990; WHO, 1990). The ultimate result of flooding is high aqueous and biotic mercury concentrations leading to potential exposure via drinking water or fish ingestion.

Background concentrations of mercury in unpolluted waters range from 0.5-3.0 ng/l in the open ocean to 2.0-15 ng/l in coastal estuaries and rainwater. High concentrations in estuaries result from suspended solids bearing mercury being carried down rivers and settling in coastal regions (Schroeder, 1989).

6.2.1 Aquatic Chemistry

Because the different physical and chemical forms of mercury have significantly different properties, the speciation of mercury is the primary factor controlling its behavior, movement, and fate in aquatic ecosystems (Schroeder, 1989).

Elemental mercury (Hg^0) which is deposited from the atmosphere has low water solubility, but under aerobic conditions it is quickly oxidized to the more soluble divalent form (Hg^{++}) (Schroeder et al., 1991; USDHHS, 1992). The typical oxidizing agents in water (in order of decreasing oxidizing strength) are oxygen, nitrate, nitrite, ferric hydroxide, ferric phosphate, sulfate, sulfur, carbon dioxide, and bicarbonate. Divalent mercury can undergo one of the following processes:

- Divalent mercury can be methylated by microbes and absorbed by biota (Iverfeldt and Lindqvist, 1984; WHO, 1976, 1990; USDHHS, 1992).

- Microbes or free radical electrons associated with dissolved humics can reduce Hg^{++} to Hg^0, which can then volatilize (Iverfeldt and Lindqvist, 1984; WHO, 1976, 1990; USDHHS, 1992).

- Divalent mercury can be photochemically reduced to Hg^0. This reaction is accelerated in the presence of humics which absorb light energy and transmit it to the bound mercury species (Iverfeldt, 1988).

- Soluble mercury species, such as $HgCl_2$ can be reduced via biotic or abiotic processes to Hg^0, which can then volatilize (Alberts et al., 1974; Xiao et al., 1991).

- Under anaerobic conditions, particle-bound mercury can be converted to insoluble HgS which precipitates to the sediment. Once sorbed, inorganic bound mercury does not readily desorb; however, severe perturbation under aerobic conditions can lead to oxidation and remobilization of a fraction of HgS from the sediment (Iverfeldt and Lindqvist, 1984; WHO, 1976, 1990; USDHHS, 1992).

- In the presence of H_2S, methylmercury will form $(CH_3Hg)_2S$ which in turn decomposes to HgS, which precipitates and deposits onto the sediment and $(CH_3)_2Hg$, which volatilizes. This process reduces the bioavailability of mercury (Bodek, et al., 1988; Winfrey and Rudd, 1990).

The distribution of these reactions depends on the redox potential and pH of the water as well as on the amount of dissolved organic carbon. In general, acidic conditions facilitate the formation of soluble mercury complexes (e.g., $HgCl_2$, CH_3Hg), while alkaline conditions facilitate the formation of volatile mercury complexes (e.g., Hg^0, $(CH_3)_2Hg$) (WHO, 1976; Iverfeldt and Lindqvist, 1984; Bodek et al., 1988; WHO, 1990; USDHHS, 1992). In seawater, mercury exists predominantly in chloro complexes, while in freshwater the mercury species are principally comprised of chloro and hydroxo complexes, in various proportions depending on the pH of the system. The half-life of mercury in water can range from minutes to years depending on the species which are present in water (Sorensen et al., 1990).

6.2.2 Effect of Lake Acidification

Over the last several decades, anthropogenic emissions have not resulted in significantly higher mercury releases or deposition to water (Lindberg et al., 1987).

However, the effect of lake acidification on the biogeochemistry of mercury in water has resulted in increased health risk concerns. For example, Lindqvist and Schroeder (1989) studied several Swedish lakes and reported that although no emission source had been situated near the lakes, concentrations of methylmercury in fish had continued to increase. They suggested that this effect was due to greater mobility and bioavailability of mercury species resulting from perpetual acidification of the environment. Increases in the concentration of methylmercury are reason for concern because methylmercury (CH_3Hg^+) is one of the most poisonous forms of mercury and is the form which is mainly bioaccumulated (USEPA, 1984; Lindqvist and Schroeder, 1989; WHO, 1990; USDHHS, 1992).

There are several mechanisms which have been suggested by which decreased pH results in increased methylation and subsequent bioaccumulation of mercury:

- Increased oxidants in the atmosphere result in more oxidation of elemental mercury to soluble species which are wet or dry deposited to lakes and other bodies of water. This increases the amount of mercury available for methylation (Lindberg et al., 1987).

- Acidification of precipitation water can increase the leaching of mercury from soils, and lead to higher mercury in surface runoff or groundwater flow (Lindberg et al., 1987).

- Low pH can reduce the binding of mercury cations to humic acids as well as cause humics to precipitate out of solution. This may make previously bound mercury available for methylation.

- Lower DOC levels resulting from acidification will decrease the role of humics as electron donors in the reduction of Hg^{++} to volatile Hg^0 (Winfrey and Rudd, 1990).

- Reduced volatilization increases the availability of mercury for methylation (Winfrey and Rudd, 1990).

- Low pH waters stimulate microbial production of methylmercury at the sediment/water interface (Wiener and Stokes, 1990).

- Low pH conditions favor the production of soluble and bioavailable monomethylmercury over volatile dimethylmercury (Bodek et al., 1988; Winfrey and Rudd, 1990; WHO, 1990).

Microbial methylation of mercury can occur either in the water column or at the sediment-water interface (Winfrey and Rudd, 1990). Although the rate of methylation is highest at the sediment water interface, the majority of methylmercury production occurs in the water column which has a high volume. Finally, it is noted that the relative impact of acidification on methylation at the sediment-water interface *vs.* in the water column is a question yet to be resolved (Winfrey and Rudd, 1990).

6.2.3 Influence of DOC Levels

The ability of mercury to undergo the reactions discussed above is largely determined by its binding to dissolved organic carbon (DOC) in the form of humic and fulvic acids. Binding of mercury and methylmercury to terrestrial DOC facilitates its transport into lakes via surface runoff (Lee and Iverfeldt, 1991). In addition, sorption of inorganic mercury complexes to suspended solids or DOC at the soil-water interface increases the mobility of mercury.

Once in the water, binding of mercury to humic substances enhances the "apparent solubility" and decreases the evaporative loss of inorganic and organic mercury complexes (Miskimmin, 1991). In addition, binding with DOC increases the ability of mercury to persist in the water column and resist sedimentation. This also results in increased mercury bioavailability (Sorenson, et al., 1990; Miskimmin, 1991; Lee and Iverfeldt, 1991). For example, Miskimmin (1991) reported a direct correlation between elevated mercury concentrations in fish and high DOC levels. He further reported that increasing DOC concentration resulted in a decreased K_d (sediment/water partition coefficient).

6.3 Mercury in Soil and Sediment

Soil and sediment can affect the distribution of mercury in the environment in two main ways: (1) soil and sediment can act as a source of mercury to surrounding media, (e.g., volatilization of mercury from soil to air, runoff of mercury containing soil into water, uptake of mercury containing sediment by biota); and (2) soil and sediment can also act as a sink for surrounding media, (e.g., atmospheric deposition to soil, settling of mercury containing suspended solids to sediment). The relative importance and magnitude of these two roles is governed by specific environmental conditions (Andersson et al., 1990).

The mobility and deposition of mercury in soil and sediment is governed by its binding to the sulfur atoms in humic and fulvic acids. This binding can be affected by percent organic carbon, pH, redox potential, temperature, and mercury speciation (Lindqvist and Schroeder, 1989). Despite re-emission of mercury from soil and water, a substantial amount of mercury accumulates in soil and sediment every year. Therefore, soils and sediments are considered as the main sinks for mercury (Sorensen et al., 1990).

6.3.1 Mercury in Soil

The soil's role as a source of mercury is derived from the fact that trace amounts of mercury occur in most rocks, particularly those high in sulfide-containing minerals. This mercury is released to the soil in the weathering process and can be augmented by several environmental factors: (1) degradation of organic materials by microbes aids in the release of complexed mercury into soil gas (Klusman and Jaacks, 1987); (2) tectonic activity can cause a significant increase in mercury accumulation in soil (Klusman and Jaacks, 1987); and (3) acidified rain increases the rate of mercury leaching from rock and the affinity of mercury for soil organic matter. It should be noted, however, that the binding to soil organic matter can lead to lower mercury concentration in porewater and, therefore, lower mobility of mercury in acidified soils (Nelson and Campbell, 1991). Once liberated from rocks, soil mercury will either bind to soil organics or volatilize to the surrounding atmosphere. The volatilization rate of mercury from soils was found to vary seasonally and to have a positive correlation with temperature (Klusman and Jaacks, 1987).

In the study of Klusman and Jaacks (1987), the concentration of elemental mercury in soil gas, measured over a 22 month period, ranged from 1.11×10^{-4} to 3.97×10^{-2} ng/L with a mean concentration of $6.22 \times 10^{-3} \pm 7.0 \times 10^{-3}$ ng/L. The concentrations were generally lowest in the winter and highest in the summer, with comparable diurnal fluctuations (high during the day and low at night).

Mercury concentrations in the humic layer have been measured to be approximately a hundred times the amount deposited to the soil surface annually (annual deposition ≈ 0.1 to 0.3 mg Hg/m^2) (Lindqvist and Schroeder, 1989). Binding of mercury to humics in the soil decreases its mobility within the soil matrix. Khan et al. (1991) reported that blockage of soil adsorption sites by organic pollutants decreased binding and, therefore, enhanced the mobility of heavy metals (including mercury) in soil.

6.3.2 Mercury in Sediment

Mercury's effective binding to organic carbon containing particles results in the majority of total mercury in aquatic ecosystems being found in the sediments (Andersson et al., 1990). This effective binding of mercury to suspended particles retards diffusion of mercury through interstitial water to overlying water, allowing the sediment to act as a significant sink for mercury.

Andersson et al. (1990) reported that at pH = 4.0 - 4.5, about 98% of mercury added to the bulk water of an aquatic system was associated with the sediments. Between 50 and 75% of the mercury in the sediments was adsorbed to humic acids, with the amount of mercury bound to deposited organic material increasing with decreasing pH. The remainder of the mercury in the sediment was associated with inorganic components of the sediment, e.g., bound to sulphides or coprecipitated with other metal oxides (such as manganese or iron). Under acidic conditions other cations present may displace mercury which is loosely bound to inorganic complexes in the sediment. Consequently, decreasing sediment pH has two discrepant effects: (1) increasing the amount of mercury bound to organic components of the sediment; and (2) decreasing the amount of mercury bound to inorganic components of the sediment. Therefore, decreasing sediment pH can have varying effects depending on the site-specific sediment composition.

Under anaerobic conditions, Hg^{++} has a high affinity for sulphide, facilitating the formation of HgS, which is insoluble and, therefore, its deposition to the sediment is enhanced. Once deposited in the HgS form, mercury is not available for methylation (Andersson et al., 1990). Although perturbations or bioturbations can re-mobilize a small percentage of HgS, deposition of HgS to sediment is considered the primary sink for mercury (WHO, 1990) (see Section 4.3).

6.3.3 Methylmercury in Soil and Sediment

Methylmercury is the most biologically active form of mercury. It is important to note that although only 0.1% of mercury deposited to the sediment is converted to methylmercury, and only 1% of total mercury is bound to fish, 49% of methylmercury in aquatic systems is found in fish (Andersson et al., 1990). Therefore, it is important to account for rates of methylation in soil and sediment.

Rates of methylation are greatest in the uppermost 1 cm of sediments and decrease substantially with depth. Little methylation occurs below a depth of 4-5 cm due to lower bacterial populations (Wiener et al., 1990; Winfrey and Rudd, 1990). The upper sediment zone of increased methylation corresponds to the areas of greatest importance for spawning and feeding of many fish (Andersson et al., 1990). Additionally, methylmercury concentrations are highest where the organic content of the sediments is highest, and there is therefore an abundance of microbes and benthic fauna.

Temperature and pH also affect the rate of bacterial methylation of mercury in soil and sediment. In freshwater lake sediments methylation is inhibited by low temperature, with optimal methylation occurring at a temperature of 35°C. This is due to the detrimental effect of low temperature on methylating bacteria (Winfrey and Rudd, 1990). At low pH an increase of methylmercury production in sediments has been observed (Andersson et al., 1990). It is believed this is due to increased protons liberating Hg^{++} from complexes via cation exchange, making it available for methylation. In addition, low pH may catalyze the enzyme transfer of methyl groups from methylcobalamin to Hg^{++} (Andersson et al., 1990).

In general, the rate of methylation varies based on the species of inorganic mercury which are present, organic content, pH, and redox potential of the soil or sediment; therefore, it is difficult to draw general conclusions about the rates (or rate constants) of mercury transformations in natural systems.

6.4 Mercury in Biota

The current body of literature suggests that the most significant human exposure pathway for mercury is via the ingestion of fish and vegetables containing methylmercury. Such exposure can result in central nervous system damage and fetal neurotoxicity (USEPA, 1984; WHO, 1990; USDHHS, 1992) (see Section 6.5). Methylmercury's toxicity is due to its lipid solubility and ability to passively diffuse through plasma membranes. Diffusion through membranes is enhanced at low pH, and is higher for cationic species of methylmercury (Boudou et al., 1991). Once inside the body, methylmercury concentrates in fat and muscle. Following adsorption, methylmercury in tissues is oxidized to reactive Hg^{++}, which is the form responsible for mercury's toxic effects (Andersson et al., 1990; USDHHS, 1992).

The net amount of biologically available methylmercury is a function of the rate of methylation, rate of demethylation, as well as processes which alter the bioavailability of methylmercury or its precursor, divalent mercury, e.g., binding to DOC or reduction to HgS (Miskimmin, 1991). Although methylmercury only comprises a minor portion of total mercury present in the environment, it is the most biologically important form of mercury. It has a high biological half-life (i.e., it persists in animal tissues) and, therefore, biomagnifies in food chains. Biomagnification is affected by bioavailability, individual growth rates, and life cycles of organisms (Andersson et al., 1990).

6.4.1 Accumulation in Microorganisms

The occurrence of methylmercury in aquatic and terrestrial ecosystems is primarily a result of microbial methylation of divalent mercury (Bodek et al., 1988; WHO, 1990; Farrell et al., 1990). Bacterial transformation of divalent mercury to volatile dimethylmercury is a mechanism of detoxification and excretion. Monomethylmercury is formed as the first step in this reaction, but under low pH may be the ultimate product (Lindqvist and Schroeder, 1989).

Suspended solids, onto which mercury species are bound in terrestrial and aquatic ecosystems, are often coated with microbial biofilms in which bound divalent mercury is converted to methylmercury. Hintelmann et al. (1993) measured the accumulation of mercury species on microbial biofilms and found that over a 14 day period divalent mercury concentrations decreased, while methylmercury concentrations increased, indicating the occurrence of microbial methylation. After 14 days, some microbial demethylation and subsequent reduction to elemental mercury occurred. The measured methylmercury BCF of the microbial biofilms ranged from 20,000 to 50,000.

The toxic effect of high mercury concentrations on microorganisms is increased at low pH. Farrell et al. (1990) studied the effect of pH on LC_{50} of methylating bacteria and found that a decrease in soil pH from 8.0 to 6.0 resulted in a decrease in the LC_{50} from 20 μg/mg to 5 μg/ml. Furthermore, speciation affected toxicity, with cationic complexes being more toxic than anionic or neutral complexes. This difference was due to the increased diffusivity and affinity of cationic species for binding sites on bacterial cell surfaces. Therefore, at low pH toxicity may reduce microbial production and bioconcentration of methylmercury.

6.4.2 Accumulation in Animals

The predominance of inorganic mercury in aquatic systems results in the majority of mercury absorbed by primary consumers, such as plankton and suspension feeding bivalves, being inorganic. However, the preferential accumulation of organic mercury results in methylmercury being the dominant form available for ingestion at higher trophic levels. As noted by a number of investigators, although only 1% of total aquatic mercury is in the organic form, the enhanced uptake and assimilation of organic mercury results in foodchain biomagnification (Riisgard and Hansen, 1990; Lenka et al., 1990; Saouter et al., 1991; Boudou et al., 1991). As a result, the mercury found in contaminated fish is almost exclusively methylmercury (Farrell et al., 1990), with concentrations in predatory fish measured to be 10,000 to 100,000 times the concentration in the surrounding water (WHO, 1976, 1990; USDHHS, 1992).

Saouter et al. (1991) investigated the accumulation of mercuric chloride and methylmercury by mayfly nymphs (*Hexagenia rigida*), which provide a major food source for fish at higher trophic levels. They found that after 28 days the accumulation of methylmercury from ingested sediment was 60 times greater than accumulation of mercuric chloride, with no significant inhibition of growth associated with this bioaccumulation. Since methylation is higher under anaerobic conditions, animals burrowing in anaerobic layers of the sediment may be exposed to high methylmercury concentrations. These animals are then eaten by pelagic species leading to biomagnification up the food chain. As a result, up to 85 to 95% of total mercury in aquatic animals can be methylmercury (Andersson et al., 1990).

Riisgard and Hansen (1990) reported that the rate of methylmercury uptake by mussels and fish was 15 times that of inorganic mercury. Fish accumulated organic mercury in blood cells, liver, kidney, and muscle tissue. Some transformation of organic mercury to inorganic mercury occurred in the liver; however, due to enterohepatic recirculation little of this inorganic mercury was eliminated from the body. The majority of lipophilic methylmercury passed easily through the intestinal membrane into the blood stream and was deposited in fat and muscle, resulting in 83 to 94% of total mercury measured in various organs being methylmercury. Rissgard and Hansen (1990) also measured an assimilation efficiency of ingested mercury, which is defined as the total amount of mercury accumulated in the body divided by the cumulative food dose. Inorganic mercury gave rise to an assimilation efficiency of less than 1% in all aquatic species tested, while the assimilation efficiency of methylmercury varied from 34% in mussels up to 90% in some species of fish. The efficient assimilation of methylmercury to fat and muscle and the lack of elimination resulted in increasing methylmercury concentrations with the age and size of fish.

Concentrations of mercury in lake fish are often inversely correlated with lake pH (Wiener and Stokes, 1990). For example, Wiener et al. (1990) found the total mercury concentration in perch (more than 95% of which was methylmercury) from a lake at pH 6.1 was 114 ng/g compared to 170 ng/g in perch from a lake at pH 5.6. Because fish tissues and organs do not methylate mercury, it is likely that the elevated mercury levels of fish in acidic lakes result from increased bioaccumulation of methylmercury at low pH (Winfrey and Rudd, 1990). There are several possible reasons for this increased bioaccumulation: (1) low pH water is associated with low calcium concentrations, which increase membrane permeability and subsequent uptake of methylmercury (Wiener and Stokes, 1990). This conclusion is supported by the study of Rodgers and Beamish (1983) (cited by Richman et al., 1988) who reported that uptake efficiency of methylmercury decreased from 25% to 8% with a tenfold increase in $CaCO_3$ concentration; (2) acidification of water may mobilize sediment and soil bound mercury increasing the amount available for methylation and bioaccumulation; (3) low pH favors the production of soluble monomethylmercury over volatile dimethylmercury; and (4) increased acidity may cause an increase in dissolved organic matter. The DOC can in turn act as a substrate on which methylation occurs. This methylmercury laden DOC can then act as a food source for suspension feeding organisms near the bottom of the food chain (Travis and Blaylock, 1993). At high mercury concentrations, the effects of increased acidity (discussed above) may be balanced against the aforementioned decrease in methylating bacteria (which results from the increased toxic effects of mercury on methylating bacteria at low pH).

Schmitt and Brumbaugh (1990) measured the concentration of mercury in a variety of fish and report mean concentrations to be 0.10 μg/g, with 85th percentile concentrations being 0.17 μg/g.

6.4.3 Accumulation in Plants

Accumulation of mercury in terrestrial plants involves three pathways: direct absorption of vapor phase mercury by foliage (air-to-leaf transfer), atmospheric deposition, and root uptake. Air-to-leaf transfer appears to be the dominant pathway, with only a small percent of mercury being absorbed from the soil by the roots (Travis et al., 1992). However, once absorbed, the majority of mercury is translocated to the upper plant parts. Consequently concentrations in foliage is typically several times higher than that in roots (Lindberg et al. 1992). Additionally, the lipid rich cuticles of leaves and fruit tend to concentrate lipophilic methylmercury, with the concentration being proportional to the lipid content (Travis et al., 1992). Concentrations in terrestrial plants range from 10 - 100 ppb (Travis et al., 1992).

Ribeyre (1991) reported that concentrations of mercury in whole plants were lower at a soil pH of 6 than at a soil pH of 7.5. This effect of acidification is opposite that observed in animals (see Section 6.4.2). Although this decrease in bioaccumulation with decreasing pH may be due to the toxic effects of mercury on methylating bacteria at low pH, the exact mechanism behind this observation is unclear. Ribeyre (1991) further reported that in some situations increases in temperature or photoperiod decreased the bioaccumulation of mercury in plants.

Aquatic plants which are not in direct contact with the air bioaccumulate mercury primarily via absorption from the sediment. Ribeyre et al. (1991) studied mercury bioaccumulation by four species of freshwater rooted macrophytes and found that they readily absorbed methylmercury from the sediment. Once absorbed, 85% of the absorbed mercury was fixed in the stems and leaves. Conversely, very little absorption of inorganic mercury was observed. Lenka et al. (1990) reported that bioconcentration of mercuric chloride in water hyacinth roots (*Eichhornia crassipes*) occurred and was time and concentration dependent. It was also reported that at concentrations above 0.05 mg/l mercuric chloride was cytotoxic.

6.5 Bioavailability of Mercury

6.5.1 Exposure and Bioavailability

The bioavailability of a chemical is defined as the fraction of a compound in a matrix that is released from that matrix, that can be absorbed by an organism. This absorbed chemical is then available to elicit a biological effect. The release and uptake of a chemical constitute facets of bioavailability, although its biological effect is often used as an indicator of bioavailability. Differences in the distribution and metabolism of the different mercury compounds results in differences in the bioavailability and toxicity of the different forms of mercury (elemental, inorganic, organic) (USDHHS, 1992). Since risk is considered to be a function of both exposure and toxicity, bioavailability is an important consideration in determining potential risk from contaminants (SCAQMD, 1988).

According to the USEPA (1984) and the USDHHS (1992), the general population is most likely to be exposed to mercury via ingestion of fish contaminated with methylmercury and inhalation of elemental mercury. It is believed, for example, that high concentrations of methylmercury in fish result in typical exposure via ingestion being ten to twenty times the exposure via inhalation (USEPA, 1984; Travis and Blaylock, 1993). An exception to this pattern is the case of occupational exposure, which is primarily to elemental mercury vapors (USDHHS, 1992).

6.5.2 Absorption and Transformation

Once inhaled, 100% of elemental mercury rapidly diffuses across the alveolar membranes of the lungs into the blood and is distributed throughout body (USDHHS, 1992). The main target organs for elemental mercury are the brain, kidneys, and fetus of pregnant women, with approximately 75-80% of inhaled mercury being retained by these tissues.

Unlike elemental mercury, inorganic mercury complexes are not easily absorbed through the lungs; however, they are absorbed through ingestion. However, ingestion of inorganic mercury is considered a minor exposure pathway, with the main target organ being the kidneys (USEPA, 1984, USDHHS, 1992).

Organic mercury can be absorbed via inhalation or ingestion, with volatile dimethylmercury being preferentially inhaled and soluble monomethylmercury being preferentially ingested (USDHHS, 1992). Approximately 95-100% of ingested methylmercury is absorbed into the bloodstream, compared to 0.1% for elemental mercury, 10-20% for inorganic mercury, and 7% for divalent mercury. Once absorbed, methylmercury is distributed via the blood to all tissues in the body within a matter of days (USEPA, 1984). Once in the body, organic mercury is converted to elemental mercury and has similar health effects and target organs i.e., damage to kidneys, brain, and developing fetus (USDHHS, 1992).

Langworth et al. (1991) studied environmental and occupational exposure to mercury and concluded that there was a positive correlation between consumption of methylmercury contaminated fish and increased levels of elemental mercury in the blood and serum. The most significant source of inorganic mercury in occupationally unexposed people was via dental amalgam filling. When they studied 89 chloralkali workers, occupational exposure resulted in elevated blood and serum mercury levels and overshadowed fish consumption and dental amalgams as the dominant exposure source.

The available literature suggests that dermal absorption of elemental, inorganic, or organic mercury is insignificant. Therefore, dermal exposure is generally not considered to be a significant route of mercury uptake (USDHHS, 1992).

Once absorbed, methylmercury and elemental mercury are oxidized to divalent mercury by the hydrogen-peroxide-catalase system in the liver, lung, kidney or red blood cells (USDHHS, 1992). Divalent mercury binds to sulfhydryl groups on proteins and can thus accumulate in the body (Constantinou et al., 1993). Several investigators have reported high levels of divalent mercury in tissues following exposure to elemental or methylmercury (WHO, 1990).

Differences in the toxicity of various forms of mercury are related to the ease in which they are absorbed across biological membranes. Because of its lipophilicity, elemental mercury can be transferred across the blood-brain barrier and through the placenta. The oxidation of mercury compounds to Hg^{++} increases their ability to pass through membranes and thus their persistence in the brain and kidney. Conversely, the relatively nonlipophilic inorganic mercury complexes are not readily absorbed, distributed, or accumulated in the body (USDHHS, 1992). The half-lives of mercury persistence in various organs of the human body range from 20 days to 80 days depending on the species and tissue being sampled (see Table 6-6).

The mechanism of mercury toxicity is related to the role of Hg^{++} as a free radical, which facilitates the degradation of macromolecules in the body (USDHHS, 1992). The most sensitive target organs are the kidneys and the central nervous system. Delayed neurological effects have been observed following exposure to organic mercury compounds. Because of the severe effects of mercury on developing nervous systems, prenatal exposure results in a higher risk to the developing fetus from exposure relative to adults. Similarly, there is evidence that children are especially susceptible to mercury toxicity (USEPA, 1984; USDHHS, 1992).

Alternatively, noncarcinogenic risk can be quantified using a Reference Dose (Rfd), which is defined as the maximum dose below which there is no significant risk. The Rfd for inhalation of elemental mercury has been reported to be 8.6×10^{-5} mg/kg/day (USEPA, 1993 cited by Constantinou et al., 1993; USDHHS, 1992). The Rfd for ingestion of methylmercury has been reported to be 3.0×10^{-4} mg/kg/day (USEPA, 1993 cited by Constantinou et al., 1993; USDHHS, 1992).

Table 6-6. Half-life of Mercury in Human Organs

Mercury Species	Target Organ	Half-life (days)
Methylmercury	blood	52-65(a)
Methylmercury	kidney	70
Methylmercury	whole body	71-79
Inorganic	lung	2
Inorganic	brain	20
Inorganic	blood	3-30(a)
Inorganic	kidney	60
Inorganic	whole body	42-60

(a) Half-life varies with different species of mercury complexes.

Source: USDHHS, 1992

The EPA (1984) suggests that the total intake of methylmercury should not exceed 30 μg/day for a 70 kg person in order to maintain minimal risk. This means that the maximum allowable ambient atmospheric concentrations should be below 1 $\mu g/m^3$ and the uptake due to ingestion should be on the average no more than 10 μg/day of methylmercury. Average atmospheric concentrations are currently 20 ng/m^3, but can reach levels as high as 1 $\mu g/m^3$ near emission sources (Lindberg, 1987) (see Section 6.1). Similarly, ingestion of 100 g of fish with an average methylmercury concentration above 100 ng/g can result in ingestion exposure above the minimum risk levels (Travis and Blaylock, 1993).

Palusova et al. (1991) estimated that concentrations in a variety of foods ranged from 0.6 to 120 μg/kg, with an average value of 22 μg/kg (see Table 6-7). These values translated to an average daily intake of mercury from food ranging from 3-32 μg/day depending on the season, with a mean dietary intake of 11 μg/day. These values are within the ranges which the EPA considers acceptable, but are close to the upper bound of the acceptable range (30 μg/day). Therefore, for sensitive or occupationally exposed individuals, risk may be significant.

7.0 SUMMARY AND CONCLUSIONS

When using intermedia transfer parameters to predict multimedia partitioning of a chemical in the environment, it may be useful to consider the following:

- The majority of both biogenic and anthropogenic mercury emissions are in the form of elemental mercury to the air. Anthropogenic emissions, primarily as combustion by-products of industrial processes, account for 10%-30% of total emissions. Biogenic emissions are from degassing of the lithosphere and hydrosphere.

- Partitioning and behavior of mercury in the environment is governed by its physical and chemical form.

Table 6-7. Mercury Concentrations in Food

Food	Concentration (μg/kg) Range	Median	n (Sample Size)
Leafy Vegetables	1-76	21	69
Fruiting Vegetables	0-53	12	89
Root Vegetables	0-63	13	38
Fruit	1-20	3	18
Eggs	0.6-25	8	38
Poultry	1-29	10	49
Fish Muscle	10-120	100	30
Cod Liver	2-35	14	12
Sardines	9-29	11	10
Apple	0.7-20	4	75

Source: Palusova et al., 1991

- Although solubility of mercury will vary with salinity, pH, temperature, etc., the site-specific variability of the aqueous solubility may need to be considered.

- The most significant exposure pathway is ingestion of fish contaminated with methylmercury.

- The main removal mechanisms for mercury from the air are dry and wet deposition.

- Sorption of HgS to suspended solids and subsequent deposition to sediments is the dominant sink for removal of mercury from the global cycle.

- Present correlations for bioconcentration of mercury in plants and available biotransfer factor correlations may only be suitable for an order of magnitude assessment.

- Analysis of multimedia partitioning and exposure to mercury should account for the relative distribution of different mercury species in each media.

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